DIAGENESIS AND GEOCHEMICAL STRATIGRAPHY OF UPPER PENNSYLVANIAN MADERA BRACHIOPODS NEW MEXICO

by

Yongwen Gao, M.Sc. (CSUT, China)

A Thesis submitted to the Department of Earth Sciences
in partial fulfillment of the requirements for
the Degree of Master of Science

Brock University
St. Catharines, Ontario

Dr. Uwe Brand Thesis Supervisor

ABSTRACT

Owing to the fact that low-Mg calcite fossil shells are so important in paleoceanographic research, 249 brachiopod, cement and matrix specimens from two neighboring localities (Jemez Springs and Battleship Rock), of the Upper Pennsylvanian Madera Formation were analyzed. Of which, about 86% of the Madera brachiopods are preserved in their pristine mineralogy, microstructure and geochemistry. Cement and matrix samples, in contrast, have been subjected to complete but variable post-depositional alteration. It is confirmed that the stable isotope data of brachiopods are much better than that of matrix material in defining depositional parameters. Because there is no uniform or constant relationship between the two data bases (e.g., from 0.1 to 3.0‰ for $\delta^{18}O$ and from 0.2 to 6.7‰ for $\delta^{13}C$ in this study), it is not possible to make corrections for the matrix data. Regarding the two stratigraphic sections, elemental and petrographic analyses suggest that Jemez Springs is closer to Penasco Uplift than Battleship Rock. Seawater at Jemez Springs is more aerobic, and the water chemistry is more influenced by continental sources than that at Battleship Rock. In addition, there is a relatively stronger dolomitization in the mid-section of the Battleship Rock.

Results further suggest that no significant biogenic fractionation or vital effects occurred during their shell secretion, suggesting that the Madera brachiopods incorporated oxygen and carbon isotopes in equilibrium with the ambient seawater. This conclusion is not only drawn from the temporal and spatial analyses, but also supported by brachiopod inter-generic comparison (Composita and Neospirifer) and statistical analysis (*t*-test).

CONTENTS

LIST OF FIGURES

LIST OF TABLES

TOPIC SELECTION

Since Lowenstam's pioneering work (1961), it has become quite clear that low-Mg calcite (LMC) fossil shells, such as belemnites and brachiopods, are the most stable carbonate allochems under normal Earth surface conditions. Furthermore, many authors have demonstrated that these low-Mg calcite brachiopod shells are especially useful in obtaining information on ancient ocean water chemistry and depositional environments (e.g., Brand & Veizer, 1980; Al-Aasm & Veizer, 1982; Veizer, 1983; Veizer et al., 1986; Popp et al., 1986; Brand & Morrison, 1987; Bates & Brand, 1991; Brand, 1989; 1994). Of paramount importance in the evaluation is, however, that the brachiopod shell samples must be pristine in their original mineralogy and chemistry. Using diagnostic criteria (e.g., Brand & Veizer, 1980; Veizer, 1983; Brand, 1989), the state and degree of diagenetic changes in brachiopod shell calcites can be recognized, and the best preserved or “least altered” samples can be isolated for further investigation and interpretation. Once the degree of diagenetic alteration has been determined and, if no biogenic fractionation or “vital effects” of brachiopod shell secretion have been observed, then their geochemical components should reflect deposition, isotope composition and temperature variations of the ambient seawater (cf. Lowenstam, 1961; Bates & Brand, 1991; Brand, 1989; 1994).

The Upper Pennsylvanian Madera Formation in north-central New Mexico has been selected for the present study mainly because of its rich brachiopod fauna. The research history of the Pennsylvanian rocks in New Mexico has been reviewed by Armstrong et al. (1979) and is summarized in their Table 1. From the late 1970's, many detailed geological maps and important research papers have been published, such as Sutherland and Harlow's (1973) paper on brachiopods, Mukhopadhyay and Brookins's (1976) paper on Rb-Sr geochronology and Sr isotopic composition, and Armstrong et al.'s (1979) paper summarizing the Mississippian and Pennsylvanian systems in New Mexico. Recently, Grossman et al. (1993) analyzed the isotopic compositions (O, C) of three genera of brachiopod shells from Kansas and New Mexico, and compared them with data from Texas. Earlier studies, generally, focused on regional stratigraphy (e.g., Brill, 1952; Baltz & Bachman, 1956; Sutherland, 1963; Roberts et al., 1976), geological mapping (e.g., Bachman, 1953; Bachman & Dane, 1962; Baltz, 1972), and stratigraphy of the formation (e.g., Sutherland & Harlow, 1967; 1973). Facies interpretations of the Pennsylvanian sedimentary rocks are limited (cf. Casey, 1980). So far only two studies (Mukhopadhyay & Brookins, 1976; Grossman et al., 1993) have related to the different geochemical aspects of brachiopod fossils and matrix.

The objectives of this thesis are: (1) to evaluate the state and degree of diagenetic preservation of brachiopod shells from the Upper Pennsylvanian Madera Formation; (2) to document the geochemical variation and stratigraphy from the Jemez Springs and Battleship Rock sections, trying to define the chemical and depositional differences between them; and (3) to reconstruct the paleoenvironmental conditions during Late Pennsylvanian time of north-central New Mexico.

Chapter 1

GENERAL GEOLOGY OF THE UPPER PENNSYLVANIAN MADERA FORMATION

INTRODUCTION

Pennsylvanian sedimentary rocks in New Mexico have received much attention because of their significant economic importance (e.g., coal, oil and gas). According to Armstrong et al. (1979), major outcrops of Pennsylvanian rocks are in the north-central parts of the state such as in the Sangre de Cristo, Nacimiento, Sandia, Manzano, Ladron, and Los Pinos Mountains, in the south-central part of the state such as in the Oscura, San Andres, Sacramento, Caballo, Fra Cristobol, and Robledo Mountains, and in southwestern New Mexico such as in the Black Range, Lone, and Big Hatchet Mountains. Thickness of the Pennsylvanian rocks varies from 2300 m in north-central New Mexico to 600-900 m in other areas of the state (Armstrong et al., 1979).

The Pennsylvanian rocks and fossils came from two localities, Jemez Springs and Battleship Rock, which are about 6.5 km apart (Fig. 1-1). At both sections the Madera Formation is fully exposed and the Jemez Springs Member, which is informally modified here from the earlier Jemez Springs Shale Member (cf. Sutherland & Harlow, 1967), represents the uppermost interval of intercalated shale and limestone. The stratigraphic sections are described in detail and presented in Fig. 1-2. Rock samples in this study were collected by Dr. Uwe Brand in 1992.

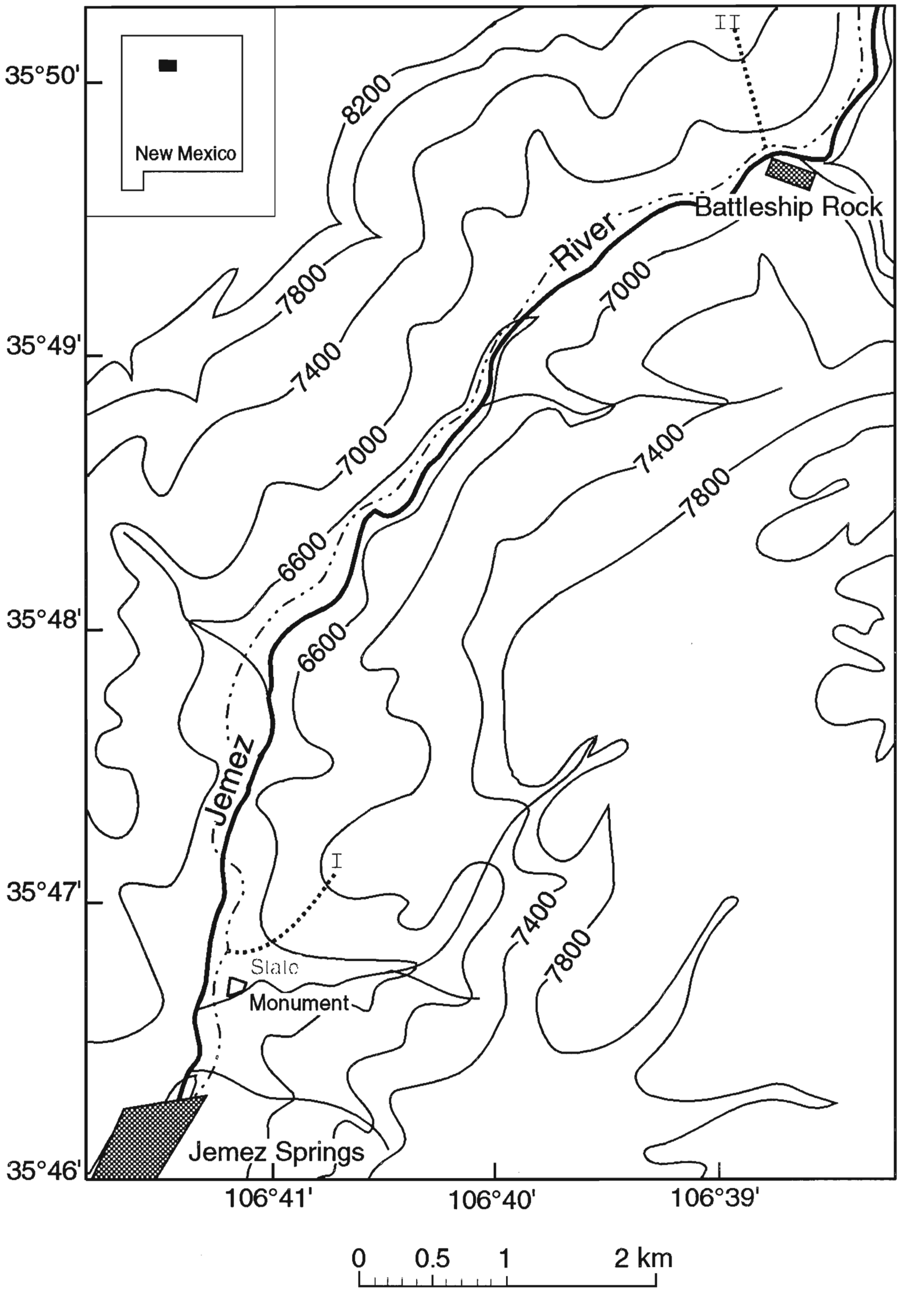


Fig. 1-1 Location map showing the two sections of the Madera Formation, New Mexico (modified from US Geological Survey, 1976).
(I - JS section; II - BR section. Topographic contours in feet)

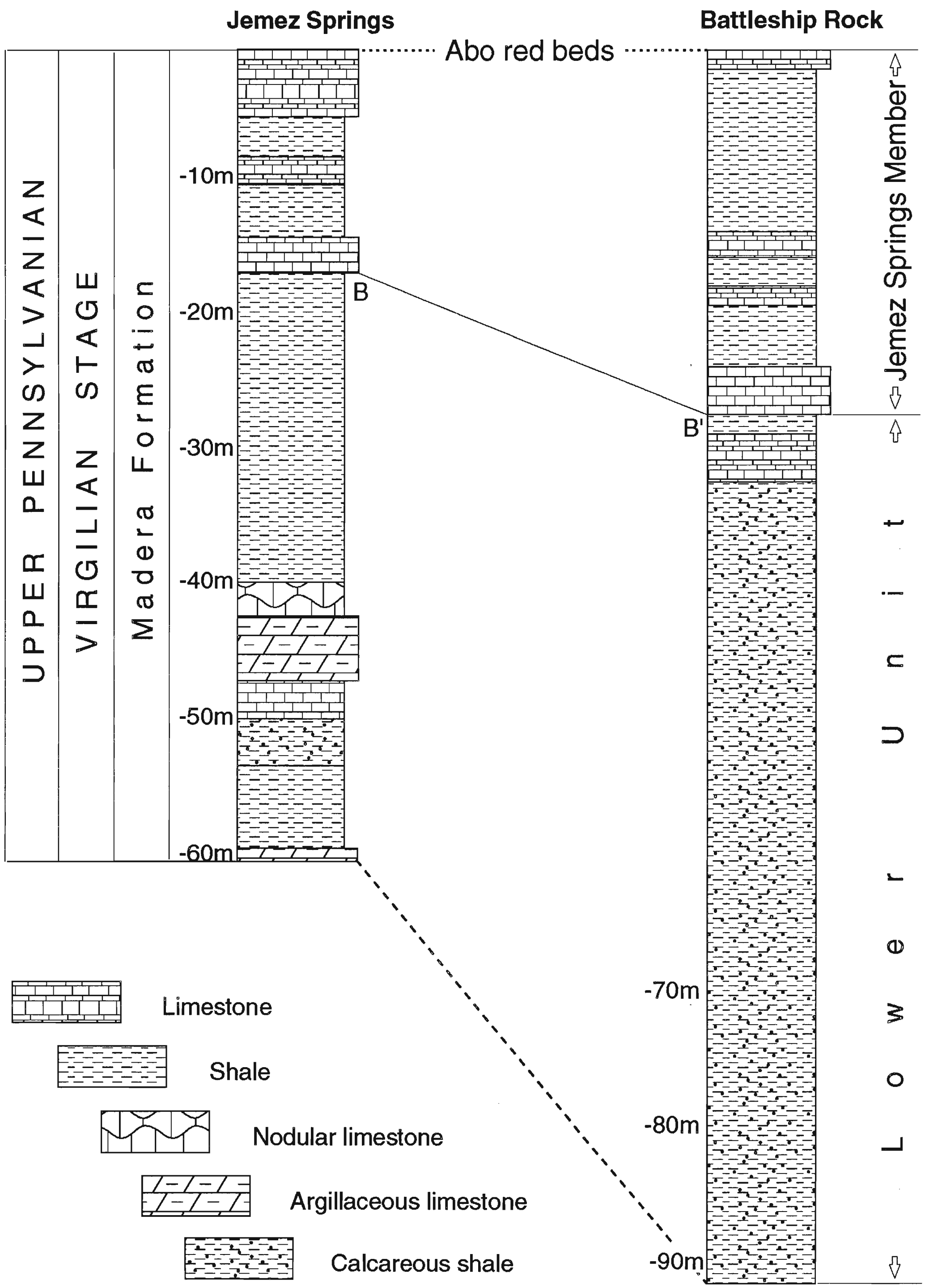


Fig. 1-2 Stratigraphy of the Jemez Springs and Battleship Rock sections, Madera Formation, New Mexico (by Brand, 1992, pers. comm.).

Jemez Springs - North of the Jemez Springs Monument (New Mexico State Highway 4) at about 1920 m above sea level in the northeast hillside, about 60 m of the Madera Formation is exposed, consisting mainly of red, grey marine limestone and grey weathering calcareous shale (Fig. 1-2). Fossils are abundant in the upper part of the section, and brachiopods consist mostly of Composita and Neospirifer (Appendix I; Sutherland & Harlow, 1967).

Battleship Rock - West of Battleship Rock (New Mexico State Highway 4) at about 2060 m above sea level on the northwest hillside, the Madera Formation is about 90 m thick (Fig. 1-2). The lower part of the section is poorly exposed and fossils are rare. Most fossil samples were collected in the upper 30 m from grey to yellow weathering shale interbedded with limestone. Three brachiopod genera, Composita, Neospirifer and Linoproductus, are present at this locality, with Linoproductus the most abundant (Appendix I).

TECTONIC SETTING

The main framework of sedimentation during Pennsylvanian time in New Mexico was dominated by subsiding basins and rising uplifts (Fig. 1-3). In the larger study area, these basins included the Paradox, Estancia, Rowe-Mora and Tucumcari Basins. The major uplifts were the Uncompahgre Uplift in the north-central part of the region; the Zuni Uplift in the west-central area; the Sierra Grande Uplift in the northeastern side; and the Pedernal Uplift extending through the central part of New Mexico. The smaller Penasco Uplift was just west of the Madera Formation outcrops along NM State Highway 4 (Fig. 1-3). Sedimentary environments in such a tectonic setting ranged from wide,

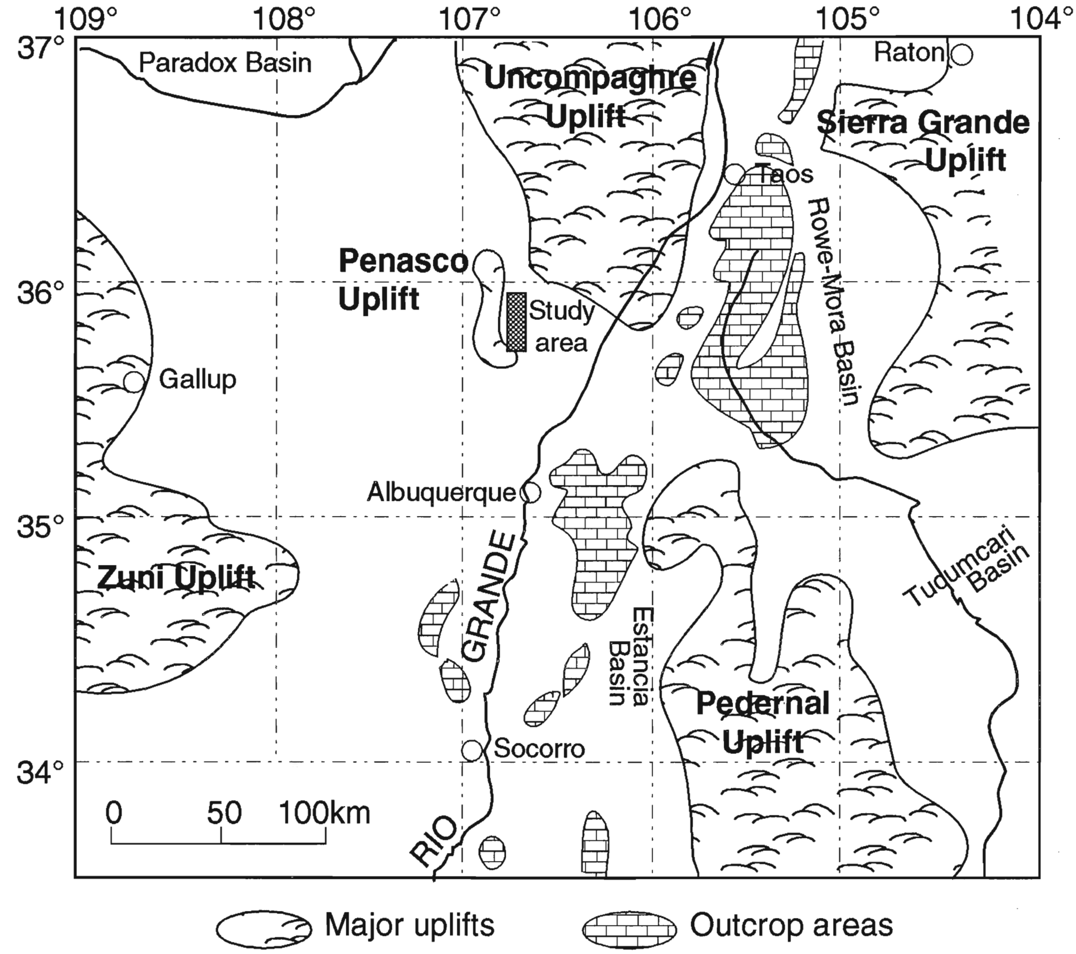


Fig. 1-3 Pennsylvanian tectonic setting of the study area, New Mexico (Modified from Armstrong et al., 1979).

tectonically stable shelves to narrow, unstable belts, with deposition of a variety of terrigenous and nonterrigenous sediments (Armstrong et al., 1979).

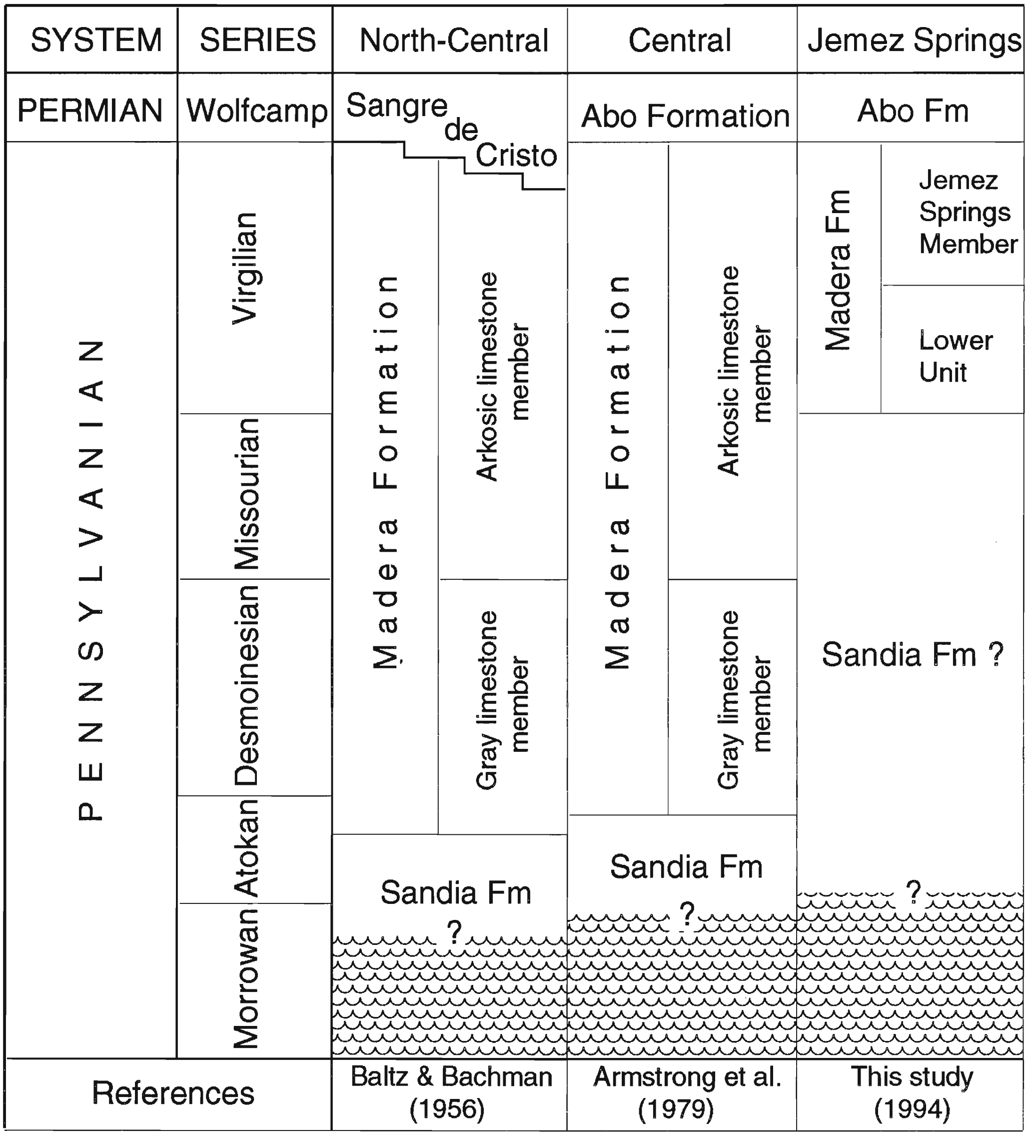
STRATIGRAPHY

Stratigraphically, the Pennsylvanian sequences unconformably overlie Mississippian sedimentary rocks (Namurian and Visean?) at most places in New Mexico, and are, in turn, conformably overlain by Permian (Wolfcampian) Abo Formation (Armstrong et al., 1979).

Gordon (1907) initially proposed the term "Magdalena Group" for all the sedimentary rocks in central New Mexico above the Mississippian and below the Abo red beds. He then divided his Magdalena Group into two formations: the lower Sandia Formation and the upper Madera Formation (Armstrong et al., 1979). Because of lateral and vertical facies variations, the regional stratigraphy of the Pennsylvanian rocks in north-central New Mexico is controversial (cf. Bachman & Meyers, 1975; Armstrong et al., 1979; Casey, 1980). The general stratigraphic classification of Pennsylvanian rocks in North-central New Mexico is summarized in Fig. 1-4.

The Madera Formation in the study area consists mainly of limestone and shale (Sutherland & Harlow, 1967; Mukhopadhyay & Brookins, 1976; Fig. 1-2). Overall, the Pennsylvanian sequence in New Mexico indicates “transgression of the sea in the Early Pennsylvanian, maximum inundation in the Middle Pennsylvanian and regression near the close of the period” (cf. Armstrong et al., 1979; p. W1). Based on stratigraphic analysis, the depositional environment of

Fig. 1-4 Stratigraphic classification of Pennsylvanian Rocks, New Mexico (system and series from Harland et al., 1990).
Note: symbols in the lower part of the diagram refer to unconformities.



the Madera Formation varies from shallow marine to near-shore marginal marine.

Sutherland and Harlow (1967) established the Jemez Springs Shale Member of the Madera Formation to include the shale below the major limestone bed underlying the Permian Abo red beds and above the regionally extensive limestone bed (cf. Fig. 1-2). In this study, this classification has been revised to be more inclusive and representative of the regionally distinctive units of the Jemez Springs valley. Thus it is proposed that the Jemez Springs Member of the Madera Formation includes the carbonates and shale below the Abo Formation and as its lower boundary the regionally extensive ledge-forming limestone bed (cf. Fig. 1-2).

Mukhopadhyay & Brookins (1976) proposed an isotopic age of 264 Ma for the Madera Formation based on Rb-Sr whole-rock studies. According to the most recent geological time scale (Harland et al., 1990), this age is slightly younger than the Carboniferous-Permian boundary. To test Mukhopadhyay & Brookins's (1976) assignment, samples covering the 60 m and 90 m exposures were evaluated for conodonts. Based on form-taxonomy of the conodonts, the Madera Formation sediments in the Jemez Springs valley are assigned a Virgilian age (cf. Fig. 1-4; von Bitter, pers. comm., 1994).

BRACHIOPOD FAUNA

Throughout most of the Pennsylvanian sections in New Mexico, marine invertebrate fossils are abundant (Gehrig, 1958; Armstrong et al., 1979). They provide the basis for the correlation of stratigraphic units. In the study area, "... the lower and middle parts of the Pennsylvanian sequence contain moderately well developed brachiopod faunas, but it is only from beds of Virgilian age that abundant specimens of exceptional preservation have been collected " (cf. Sutherland & Harlow, 1967; p.1065).

From the Jemez Springs Member of the Madera Formation (cf. Fig. 1-4), Sutherland and Harlow (1967) collected and described 18 brachiopod species, representing 17 genera. Certain brachiopod genera such as Lingula, Rhipidomella, Meekella, Lissochonetes and Wellerella, which are common elsewhere in Upper Pennsylvanian rocks of New Mexico (cf. Sutherland & Harlow, 1967), are absent.

SUMMARY

The fossiliferous Pennsylvanian sedimentary rocks in north-central New Mexico can be divided into two formations: the Sandia Formation and the overlying Madera Formation. The Madera Formation conformably overlies the Sandia Formation and is conformably overlain by Permian red beds of the Abo Formation. The lower unit of the Madera Formation is characterized by light-grey limestone, and the upper part, mainly the Jemez Springs Member in this study, is composed of limestone, shale and calcareous shale.

Chapter 2

MICROSTRUCTURE OF BRACHIOPOD SHELLS FROM THE MADERA FORMATION

INTRODUCTION

The term “Microstructure” has been well understood in metallographic studies for a long time, but it has been popularized only recently in the area of sedimentary carbonates, especially since the commercial debut of SEM (scanning electron microscopy) in the late 1960's (Trewin, 1988).

In clay mineralogy, Bennett et al. (1977; 1991) and Bennett and Hulbert (1986) recognized three dominant processes and mechanisms that affected the development of clay microstructure, i.e., (1) physicochemical, (2) bio-organic, and (3) burial diagenesis. In this study, the microstructure of fossil shells or skeletons is defined as the arrangement of fine crystalline units which is visible at SEM magnifications and can be treated as the "mirror-image" of either formational or diagenetic processes depending on the degree of preservation. Because microstructural patterns of fossil shells or skeletons may be modified by diagenetic processes, which can be analyzed by SEM, these high-resolution observations have provided important information for carbonate diagenesis study. Therefore, microstructures from low-Mg calcite (LMC) brachiopods are essential in understanding the nature, degree and history of the diagenetic alteration.

Bates (1989) reviewed the shell structures in both modern and Paleozoic brachiopods. An articulate brachiopod shell is composed of a thin outer organic periostracum underlain by primary and secondary calcite layers (cf. Milliman, 1974; Bathurst, 1976; Rowell & Grant, 1987; Bates, 1989). Only the primary and secondary layers are usually recognized in fossils because the thin organic periostracum is rarely preserved. As well, the different status of preservation among brachiopod genera may largely be dependent on shell architecture (e.g., shell thickness, surface morphology and ornamentation; Brand, 1994). During SEM observation, mostly the secondary layer of brachiopod shell structures was recognized because weathering and laboratory cleaning of specimens usually removes the primary prismatic calcite layer (cf. Fig. 3-15D).

SEM METHOD

Selected brachiopod shell fragments were first viewed under a WILD - Heerbrugg binocular microscope, in order to identify dominant features on the fresh broken surfaces such as shell fiber, porosity and ornamentation. Specimens were then mounted on 10 mm diameter stubs using Harbutt's Plasticine. To eliminate electric-charge effects and to obtain good resolution, mounted samples were coated with gold/palladium using an ISI PE-5000 Sputter Coater supported by argon gas. The thickness of the gold coating is normally about 500 Å.

A total of 68 shell fragments were examined on a Super MINI-SEM® (International Scientific Instruments) equipped with a Polaroid camera. The effective working magnification by this machine was 20~5,000x. Samples were chosen to cover the full range of the Jemez Springs and Battleship Rock sections, stratigraphic facies and fossil shells (e.g., Composita, Neospirifer, Linoproductus, and crinoids). SEM examinations were performed on both perpendicular and cross-sectional surfaces. Unfortunately, because of technical difficulties and eventual breakdown of the machine, not every sample produced photographs of adequate quality.

RESULTS

Results of the SEM analysis and preservation status of the Madera brachiopods are summarized and presented in Table 2-1.

The majority of shell samples are well preserved with respect to their original microtexture. Although, some stratigraphic variations in brachiopod preservation might be expected, no distinct trend was identified to support such an idea (Table 2-1). The three major brachiopod genera (i.e., Composita, Neospirifer, Linoproductus), however, do exhibit apparent differences in state and degree of preservation of their shells. The decreasing order of shell preservation is approximately Neospirifer → Composita → Linoproductus.

Table 2-1 SEM analysis of Jemez Springs and Battleship Rock fossil shells, Madera Formation, New Mexico

#Sample	Fossil	Preservation
JEMEZ SPRINGS		
UL-2C	Composita	Altered
UL-4D2	Neospirifer	Preserved
UL-4I	Composita	Altered
ULMMA-12A	Unidentified	Altered
ULMMA-28	Neospirifer	Preserved - minor altered
ULMMA-31	Composita	Preserved - minor altered
ULMMA-34B	Neospirifer	Preserved
BATTLESHIP ROCK		
BR-22A	Neospirifer	Altered
BR-31	Linoproductus	Altered
BR-34A	Linoproductus	Preserved
BR-39	Composita	Preserved
BR-41A	Neospirifer	Preserved
BR-43	Neospirifer	Preserved
BR-47B	Linoproductus	Altered
BR-48B	Linoproductus	Altered
BR-53B	Composita	Preserved
BR-55A	Linoproductus	Altered
BR-57	Composita	Preserved
BR-59	Crinoid	Altered
BR-65	Neospirifer	Preserved - minor altered
BR-67	Composita	Altered
BR-68B	Composita	Preserved - minor altered

Figure 2-1 displays a range of alteration in Jemez Springs brachiopods. Figs. 2-1A, B and C show sharp trabecular fibers and no evidence of any diagenetic alteration, representing pristine microstructural features. Figs. 2-1D, E and F show different degrees of alteration of keeled fibers within the secondary layer of shells. Cementation (Figs. 2-1D and E), dissolution and diagenetic transformation of original LMC occurred in conjunction with replacement by diagenetic low-Mg calcite (dLMC) such as equigranular calcite, resulting in secondary porosity (Fig. 2-1F).

Additional microstructural features of Jemez Springs brachiopods are presented in Figure 2-2. Fig. 2-2A shows trabecular fibers in the secondary layer of a Neospirifer. Some of the fibers have been cemented by diagenetic low-Mg calcite. Figs. 2-2B, C, D and E depict sharp keeled fibers either in Neospirifer or in Composita, indicating well-preserved microstructures. Fig. 2-2F, however, shows complete replacement of original trabecular fibers of the secondary layer by diagenetic granular calcite. It is worth noting that this range of alteration occurred not only throughout the stratigraphic section, but also in a single shell. For instance, in sample MMA-28, a Neospirifer, everything from pristine trabecular fibers (Fig. 2-2B), minor cementation (Fig. 2-2A) to extensive cementation and alteration (Fig. 2-1D) was observed. Similar degree of alteration is also noted in Composita of specimen MMA-31 (Fig. 2-1B, E and Fig. 2-2C). Since it is possible to find a range of degrees of alteration within a single shell, only the region with preserved microstructures would most likely have geochemical contents reflecting depositional conditions.

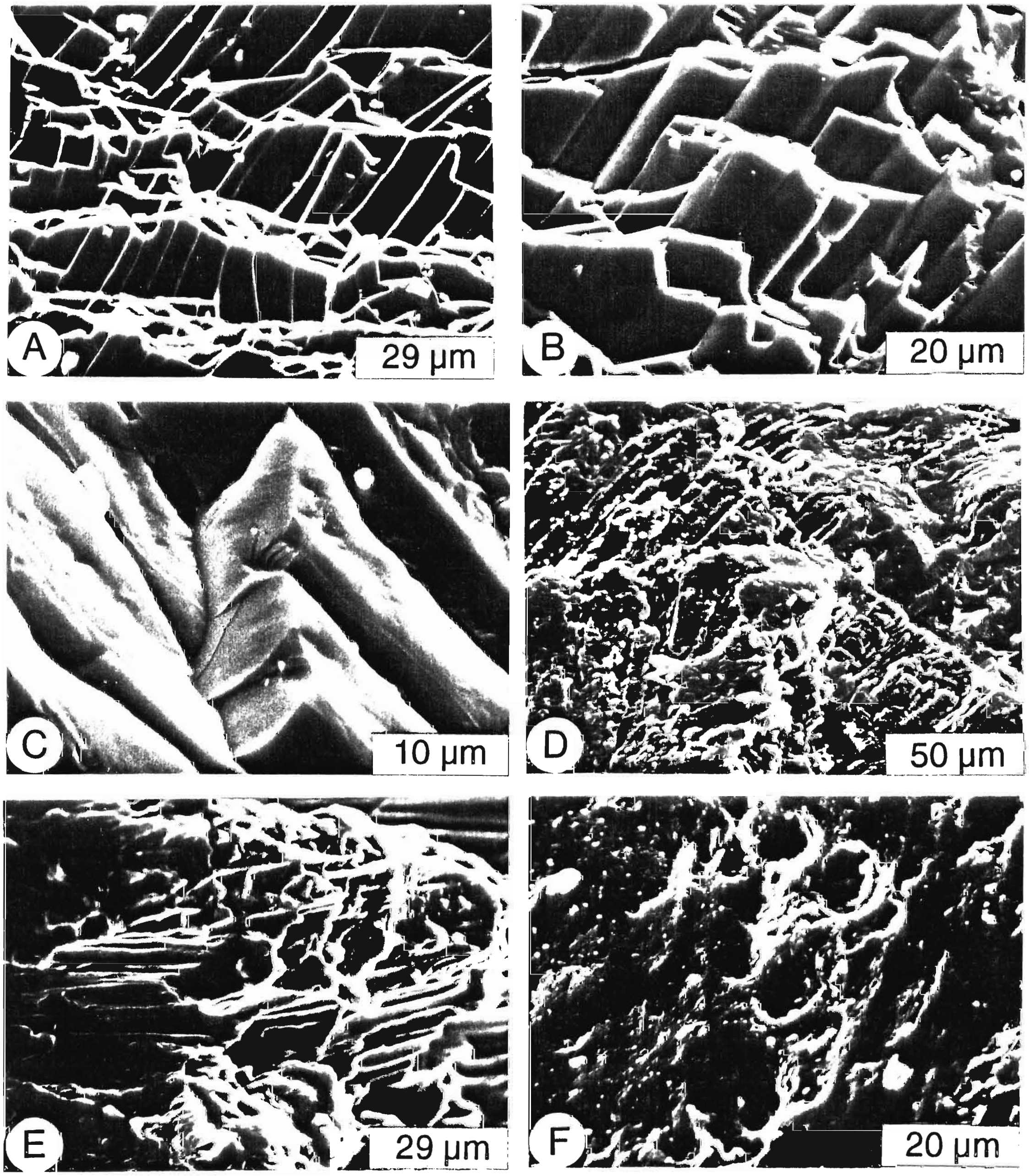


Fig. 2-1 SEM photographs showing a range of diagenetic alteration in brachiopods from the Jemez Springs section, Madera Formation

Plate A,	MMA-34B,	Neospirifer;
B,	MMA-31,	Composita;
C,	UL-4D2,	Neospirifer;
D,	MMA-28,	Neospirifer;
E,	MMA-31,	Composita;
F,	UL-4I,	Composita.

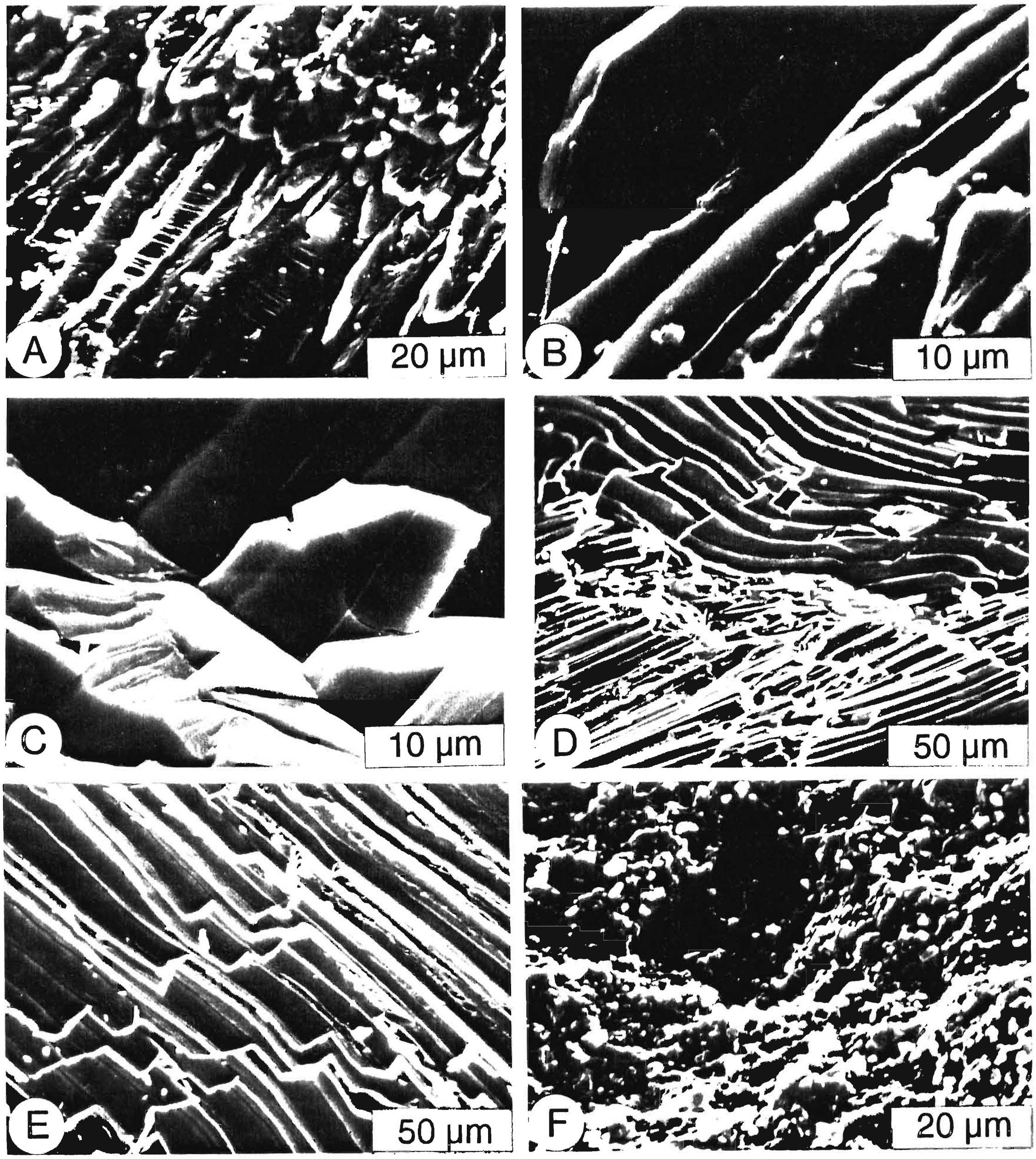


Fig. 2-2 Additional SEM photographs of microstructures in brachiopods from the Jemez Springs section, Madera Formation

Plate A,	MMA-28,	Neospirifer;
B,	MMA-28,	Neospirifer;
C,	MMA-31,	Composita;
D,	MMA-34B,	Neospirifer;
E,	UL-4D2,	Neospirifer;
F,	UL-2C,	Composita.

Figure 2-3 contains SEM micrographs of brachiopods and crinoids from Battleship Rock, also displaying a range of alteration in microstructural features. Figs. 2-3A and B show the sharp keeled fibers with no or minor diagenetic alteration. Fig. 2-3C, one of the best preserved specimen of Linoproductus observed in this study, displays some cementation or minor degree of alteration. Figs. 2-3D, E, nevertheless, shows extensive alteration such as cementation, dissolution and replacement. For the crinoid specimen (Fig. 2-3F), some remnants of the stereome are still preserved, while in most instances the stroma has been filled by syntaxial diagenetic cement (Bathurst, 1975). Subsequently, some of the stromal space was filled by euhedral dolomite rhombs.

Figure 2-4 shows additional SEM micrographs of brachiopods from Battleship Rock. Figs. 2-4A and B reveal original trabecular fibers within the shells of Composita and Neospirifer, respectively. Fig. 2-4C shows two kinds of microstructures: preserved keeled calcite fibers (in the lower part), and diagenetic dissolution and replacement (in the upper part). In Fig. 2-4D, a Linoproductus, exhibits extensive diagenetic alteration of calcite crystallites.

More SEM micrographs which show the range of diagenetic alteration from the Battleship Rock brachiopods are depicted in Figure 2-5. Figs. 2-5A and C show the pristine trabecular fibers, and some secondary dissolution features. Figs. 2-5B and D show an intermediate degree of diagenetic alteration. Lastly, Figs. 2-5E and F show the extensive alteration of Linoproductus and Neospirifer specimens, represented by cementation, dissolution and replacement.

In conclusion, SEM micrographs reveal varying degrees of preservation of the Madera brachiopods. Alteration of fibrous layers ranges from well-

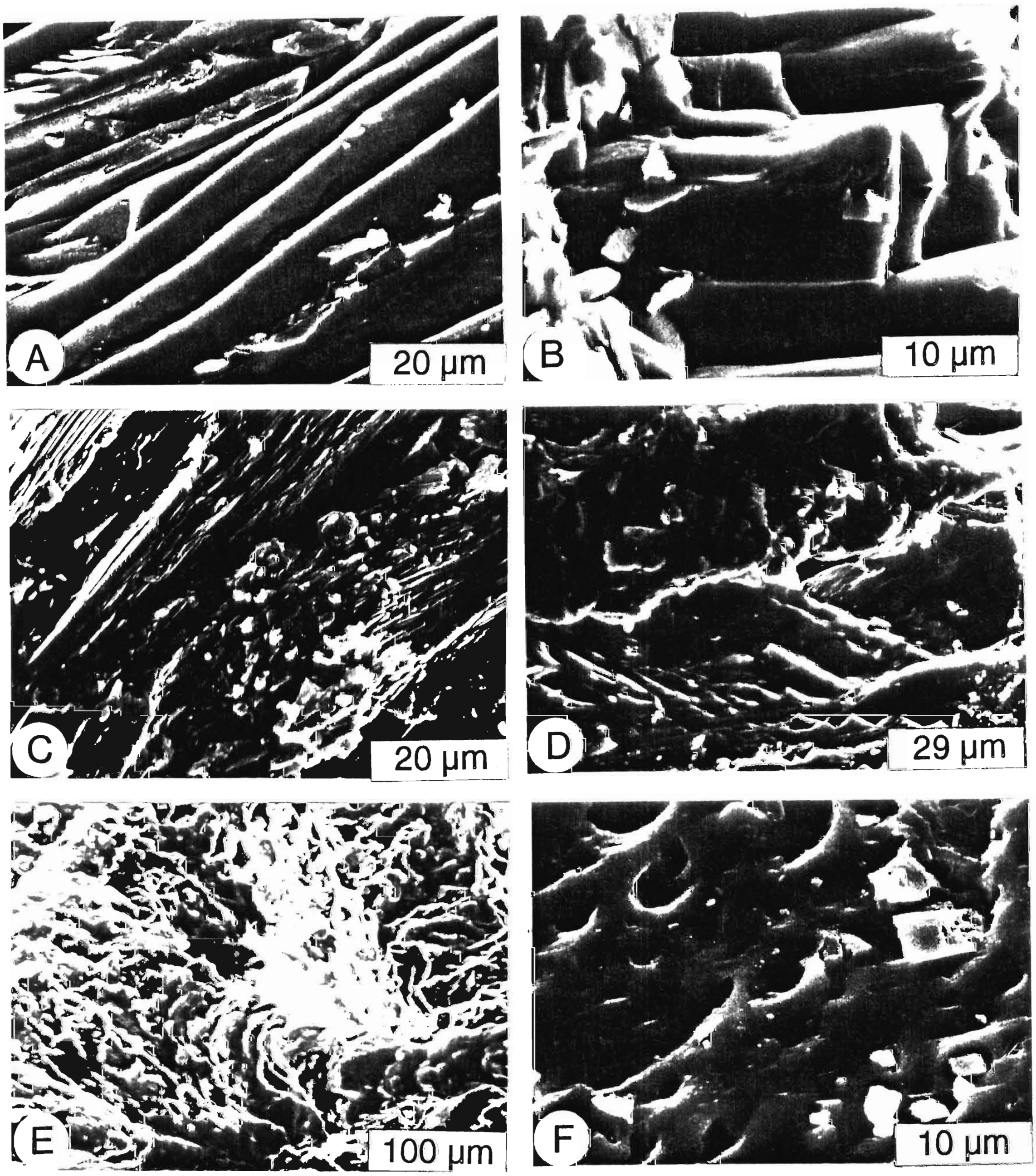


Fig. 2-3 SEM photographs showing the range of diagenetic alteration in brachiopods and crinoids from Battleship Rock section, Madera Formation.

Plate A,	BR-57,	Composita;
B,	BR-43,	Neospirifer;
C,	BR-47B,	Linoproductus;
D,	BR-68B,	Composita;
E,	BR-67,	Composita;
F,	BR-59,	Crinoid.

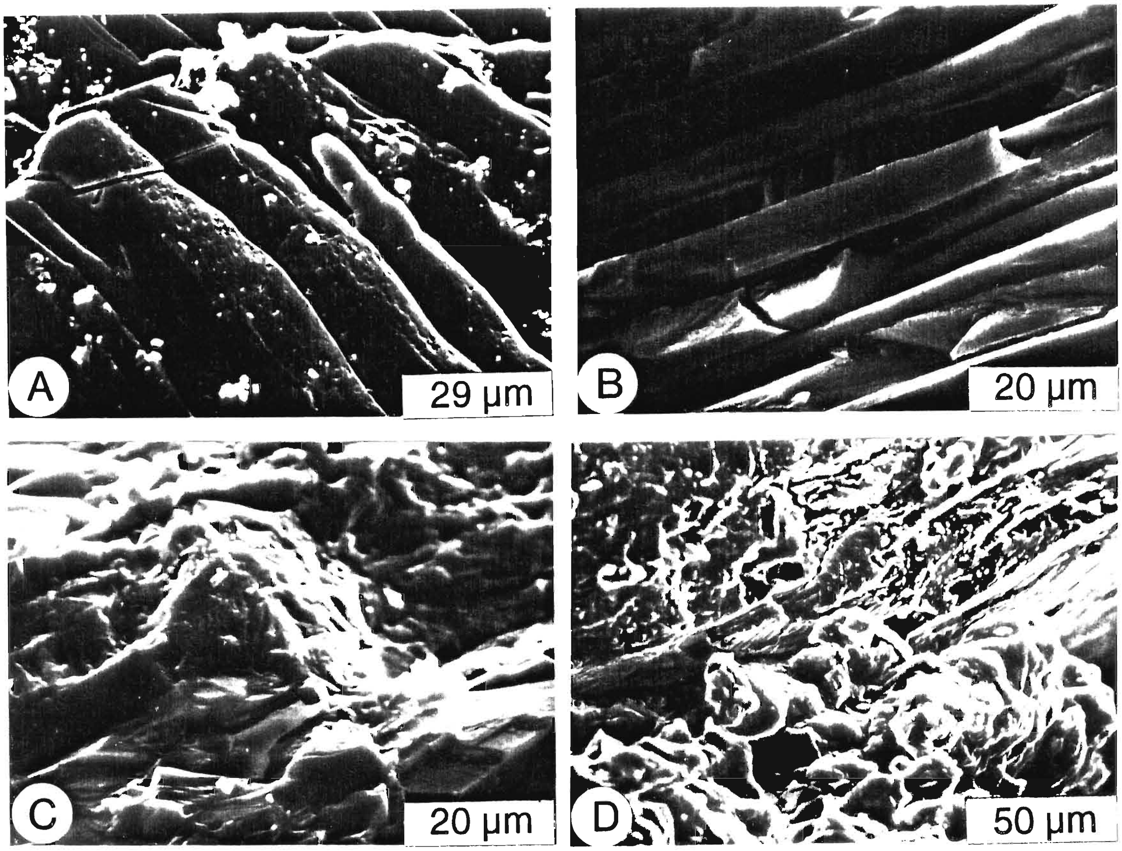


Fig. 2-4 SEM photographs of microstructures in brachiopods from the Battleship Rock section, Madera Formation

Plate A,	BR-39,	Composita;
B,	BR-41A,	Neospirifer;
C,	BR-67,	Composita;
D,	BR-47B,	Linoproductus.

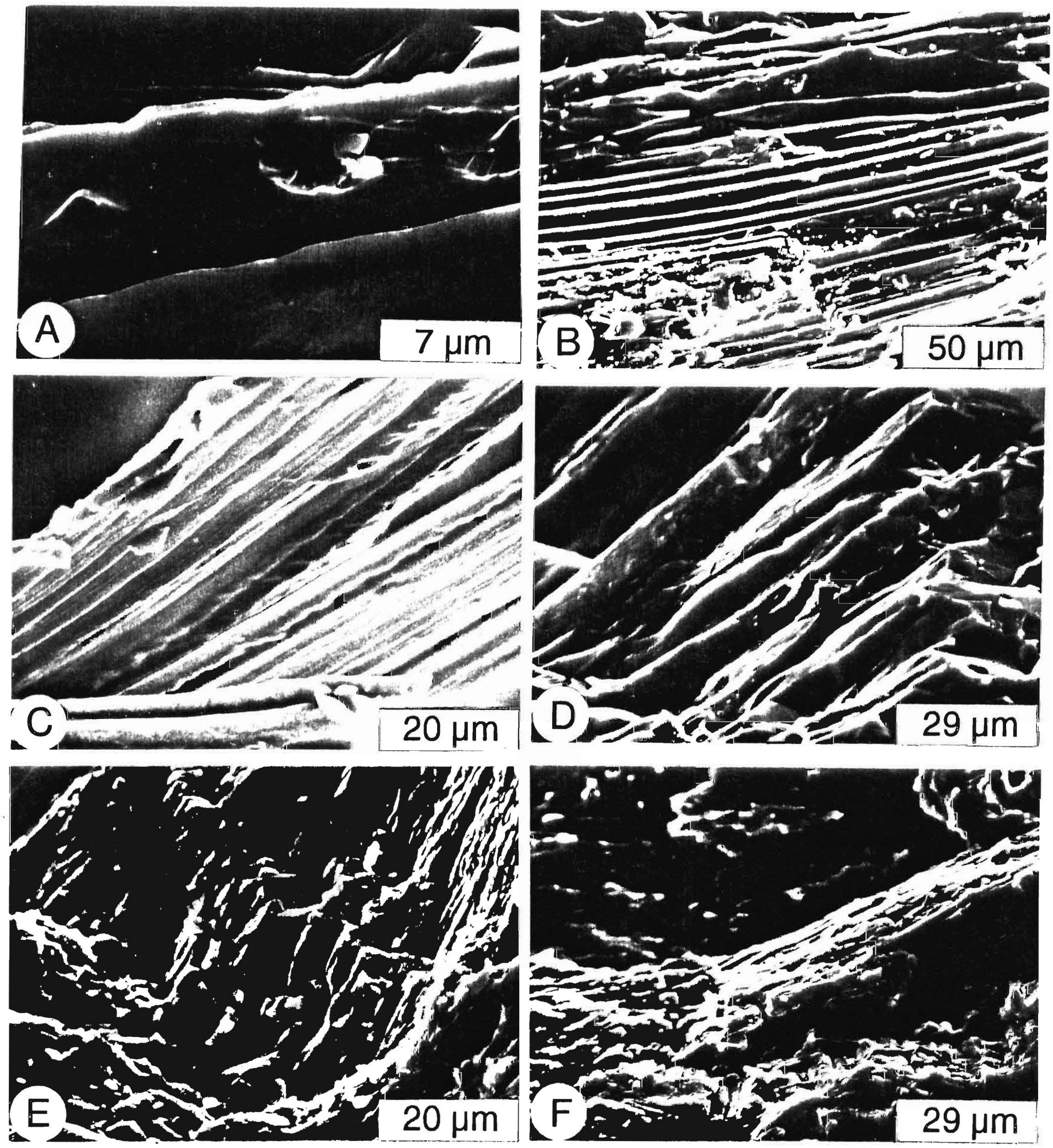


Fig. 2-5 SEM photographs of microstructures in brachiopods from the Battleship Rock section, Madera Formation

Plate A,	BR-41A,	<u>Neospirifer</u>;
B,	BR-43,	<u>Neospirifer</u>;
C,	BR-53B,	<u>Composita</u>;
D,	BR-53B,	<u>Composita</u>;
E,	BR-31,	<u>Linoproductus</u>;
F,	BR-22A,	<u>Neospirifer</u>.

preserved, slight dissolution or minor alteration, to extensive obliteration of pristine shell microstructures and crystallites.

SUMMARY

Microstructural analysis on brachiopod shells from the Madera Formation has shown there are varying degrees of preservation and a range of diagenetic alteration. The degree and range of alteration have been observed not only within the two stratigraphic sections (both Jemez Springs and Battleship Rock), but also within single fossil shell. Among three brachiopod genera, Neospirifer and Composita shells are on the whole well preserved, showing pristine microstructural features such as sharp trabecular or keeled fibers in the secondary layers.

Chapter 3

ELEMENTAL GEOCHEMISTRY OF BRACHIOPODS FROM THE MADERA FORMATION

INTRODUCTION

Carbonates consist of three major minerals: rhombohedral calcite and dolomite, and orthorhombic aragonite. According to their Mg contents, calcites are then subdivided into three varieties: low-Mg calcite (LMC, 0-4 mol% $MgCO_3$), intermediate-Mg calcite (IMC, 4-7 mol% $MgCO_3$), and high-Mg calcite (HMC, >7 mol% $MgCO_3$). Of these, LMC is the most resistant carbonate to dissolution and diagenesis (cf. Chave, 1954; Milliman, 1974; Brand, 1994).

The precipitation and subsequent dissolution-reprecipitation of calcium carbonate can be described as:

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^- \qquad (3\text{-}1)$$

During this process minor and trace elements are incorporated into carbonate mineral phases by substituting for Ca^{2+} in the crystal structure. Trace elements with larger ionic radii, such as Sr^{2+} and Na^+, are preferentially incorporated into orthorhombic aragonite, whereas rhombohedral calcite is enriched in smaller ions, such as Mg^{2+}, Fe^{2+}, Mn^{2+}, Zn^{2+} and Cd^{2+}. This substitution is governed by a distribution coefficient (D) of a specific trace element between liquid and solid phases which can be expressed by:

$$({}^{m}Me / {}^{m}Ca)_{S} = D \; ({}^{m}Me / {}^{m}Ca)_{L} \qquad (3\text{-}2)$$

at equilibrium (i.e., constant temperature and pressure) and no concentration gradients between the phases (McIntire, 1963; Veizer, 1983). In equation 3-2, Me represents the minor and/or trace element expressed in moles (m) in the solid (S) and liquid (L) phases. At non-equilibrium conditions, however, the relationship will change into:

$$\log ({}^{m}Me_{I} / {}^{m}Me_{F}) = D \; \log ({}^{m}Ca_{I} / {}^{m}Ca_{F}) \qquad (3\text{-}3)$$

where I and F are the initial and final concentrations of minor/trace elements and Ca in solution (Gordon et al., 1959; Veizer, 1983).

In the case when D=1, the carbonate will incorporate Me in equilibrium with the aqueous phase. If D>1, the Me will be enriched in the solid phase relative to the Me/Ca of the liquid phase, whereas when D<1, the carbonate solid phase will be depleted in Me. Although partitioning of minor and trace elements into carbonates is related to certain physico-chemical conditions such as temperature, coupled substitution, and rate of precipitation, the trace element model (cf. Brand & Veizer, 1980), in conjunction with isotope incorporation into biogenic carbonates, should be useful indicators of kinetic and metabolic fractionation processes.

AAS METHOD

Fossil samples were first manually separated from their host rocks, and then cleaned by 10% HCl for about 10-15 seconds. According to their weights ($x \leq 0.150$ g; 0.150 g$<x\leq$0.200 g), sample powders were digested in 5 mL or 9 mL of 5% (v/v) HCl for 90 minutes. After rinsing of the digestion fluid through a funnel and into a volumetric flask, the solutions were brought to their working volumes of 10 mL, 25 mL and 50 mL with deionized water. Insoluble residue (I.R.) of the samples was determined gravimetrically by ashing the filter paper with residue (Whatman Ashless Filter Paper #40) at 500 °C for 2 hours. The insoluble residue of the samples ranged from 0 to 84.4%, with a mean of 19.7%. All discussions are based on elemental concentrations recalculated on a 100% (insoluble residue-free) carbonate basis (cf. Brand & Veizer, 1980).

249 samples including 132 brachiopods (Composita 50; Neospirifer 46; Linoproductus 36), 11 crinoids, 90 matrices, 11 cements, and 6 unidentified brachiopod fragments were analyzed on a Varian SpectrAA-400 Atomic Absorption Spectrometer (AAS). All samples were measured for 9 elements (Ca, Mg, Sr, Na, Fe, Mn, Zn, Cd & Pb). Of these, Ca and Mg analyses were performed in an air-acetylene flame supported by a 2.5% (v/v) HNO_3 and 10,000 ppm-La solution, whereas Na, Mn, Fe and Zn supported by a 2% (v/v) HNO_3 and 2100 ppm-K solution. Sr was determined in an acetylene-nitrous oxide flame supported by 2% (v/v) HNO_3 and 2000 ppm-K solution. Cd and Pb analyses were carried out using the graphite-furnace method on a Varian GTA-96 Graphite Tube Atomizer. Mean accuracy of the technique compared with N.B.S. (U. S. National Bureau of Standards) 634 and/or 636 and average precision based on duplicate analyses are: Ca (5.6; 3.7); Mg (5.7; 2.7); Sr (4.3;

3.0); Na (18.6; 5.8); Mn (8.2; 5.0); and Zn (11.2; 15.1) relative percent, respectively. Compilation of elemental data is reported in Appendix I. However, Pb was not used in the following discussion because of its erratic measurement.

DIAGENETIC EVALUATION

Trace element contents and their relative magnitudes of chemical displacements have been proved to be useful indicators of the state and degree of diagenetic alteration on carbonate allochems (e.g., Brand & Veizer, 1980; Veizer, 1983; Bates & Brand, 1991; Brand, 1982; 1994). It was suggested that during diagenetic equilibration of fossils and matrix there is a decrease in Sr, Na, and an increase in Mn, Fe, Zn, and possibly Mg (Brand & Veizer, 1980; Fig. 1). Other studies, such as Carpenter et al. (1991), utilized stable isotopes of abiotic marine calcite cements to elucidate their diagenetic history. In this study, fossils of brachiopods and crinoids in conjunction with their matrix and cements were examined. This should provide for a direct comparison between different mineral phases, and between biotic and abiotic carbonate allochems subjected to similar diagenetic processes.

Despite variable diagenetic impacts on the carbonate constituents of the Madera Formation, distinct chemical signatures are retained in the samples. This geochemical differentiation between the mineral phases (original LMC to IMC ~ brachiopods, IMC to HMC ~ crinoids; HMC and/or aragonite ~ cement, HMC and/or aragonite ~ matrix) suggests a complex history of post-depositional preservation and diagenetic processes. In general, Mg, Sr and Fe contents of brachiopods and crinoids from the Jemez Springs section are much lower than those from Battleship Rock (Table 3-1).

Table 3-1 Mean values of some trace elemental data from the Jemez Springs and Battleship Rock sections, Madera Formation

CATEGORY	Number	Mg (ppm)	Sr (ppm)	Na (ppm)	Fe (ppm)	Mn (ppm)	Cd (ppb)
Brachiopod	52*	1484	525	1482	146	217	303
	80	2532	682	780	304	163	1030
Crinoid	2	1952	526	1535	101	122	667
	9	6319	740	242	681	315	290
Cement	3	925	272	1217	97	1014	281
	7	4803	496	107	481	734	521
Matrix	37	2066	390	1018	379	639	731
	53	9041	712	427	1340	456	786

* The first number is from Jemez Springs, the second from Battleship Rock.

The carbonate constituents from Jemez Springs have similar Sr/Ca ratios but extremely variable Mn contents (Fig. 3-1). Brachiopods and crinoids are the most enriched in Sr and depleted in Mn, whereas matrix and cements have the highest Mn and correspondingly lowest Sr contents. Similar Sr-Mn trends and relationships have been exhibited from Battleship Rock (Fig. 3-2).

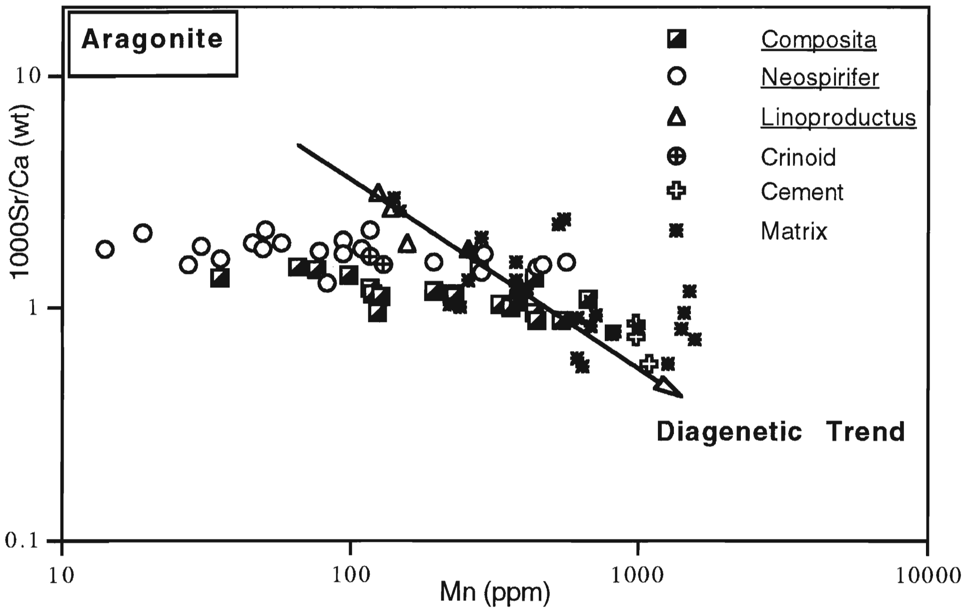


Fig. 3-1 Comparison of carbonate allochems from Jemez Springs. The diagenetic trend is for the originally aragonitic matrix and cements (Brand & Veizer, 1980). The aragonite field is based on modern aragonitic lime-mud (Milliman, 1974).

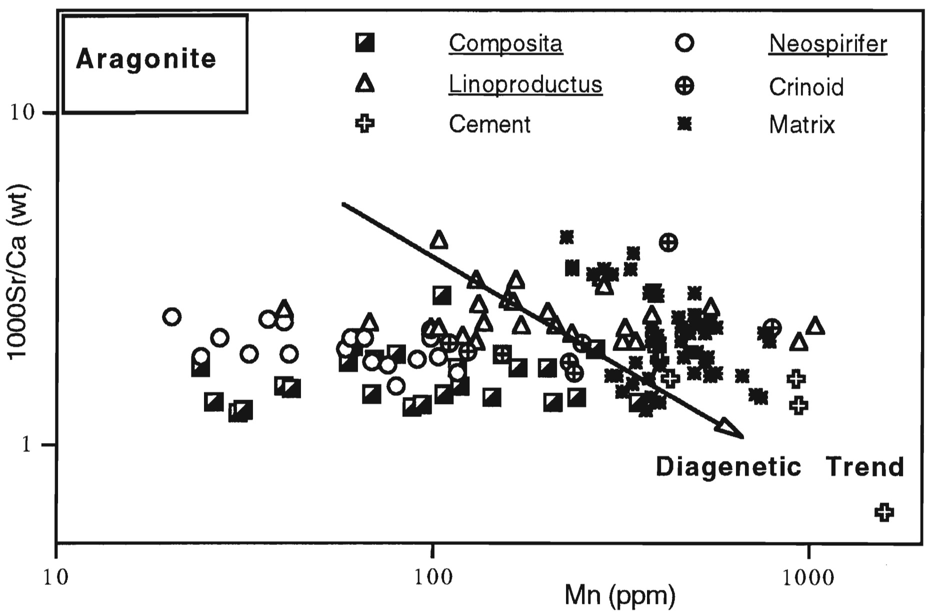


Fig. 3-2 Comparison of carbonate allochems from Battleship Rock. The trend and field as in Fig. 3-1.

Nevertheless, separate analysis of matrix and biogenic constituents shows that their general similarity is deceptive and does not reflect actual geochemical trends. Some distinctions can be seen for both the Sr and Mg contents between the matrix and cement of the two sections (Fig. 3-3). Cements

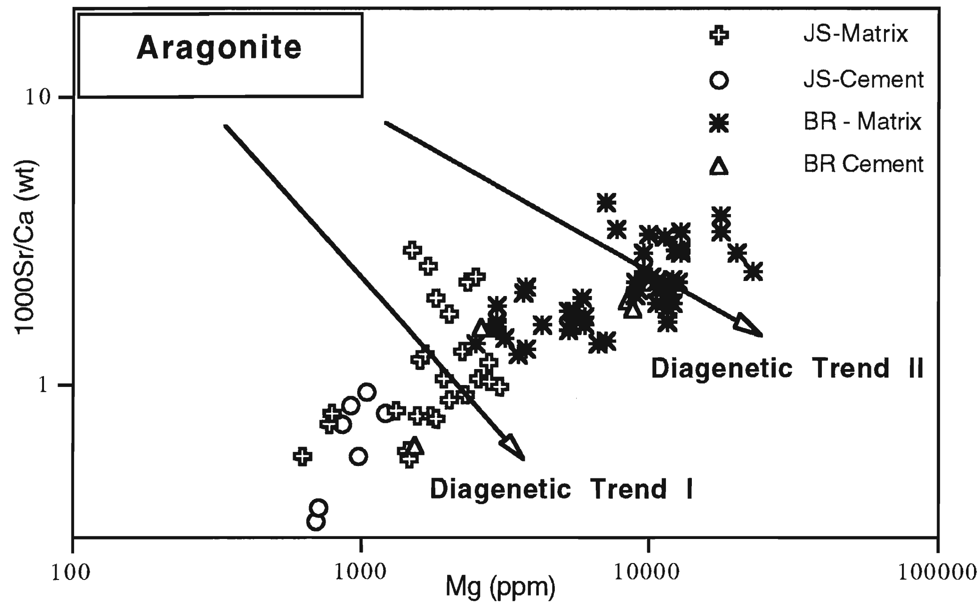


Fig. 3-3 Comparison diagram of matrix and cement from two sections of the Madera Formation. The trends and field as in Fig. 3-1.

generally have lower Sr and Mg contents than the micrite matrices. This lower elemental composition reflects a genesis distinct from that of their respective micrite matrices. Moreover, the micrite data fall into two distinct clusters in

Figure 3-3, suggesting that either environmental (depositional) or diagenetic processes or a combination of the two are responsible for the observed divergent trends.

Further evaluation of the data, horizon-by-horizon, between the two sections shows that the matrix of the Upper Madera Formation has similar Mg contents, followed by dissimilar trends through the prominent ledge-forming limestone bed and underlying sediments (Fig. 3-4). In any case, it is postulated that the prominent Mg excursion observed between -24 m and -32 m in the Battleship Rock section is related to dolomitization of the original micrite. Consequently, the dichotomous Sr content of the matrix must be related to mineralogical differences of the carbonates in the depositional environment.

The Mg contents of the cements, except for one, are all lower than their coeval micrite matrices (Fig. 3-4). This may indicate that these constituents experienced a greater degree of diagenetic alteration than their corresponding counterparts. Alternatively, there is a possibility that the low-Mg contents may be related to compositional differences in depositional mineralogy. These questions on cements, despite the extensive work by Lohmann and coworkers (e.g., Given & Lohmann, 1985), remain unanswered.

The matrix, consisting of micrite and microspar, falls well outside the Fe and Mn limits identified for modern brachiopod low-Mg calcite (mb LMC, Fig. 3-5). Such displacement in Mn and Fe, also revealed by the Sr and Mg data, suggests that this material has been subjected to post-depositional alteration, with two or more diagenetic source fluids responsible for the illustrated divergent trends (cf. Fig. 3-3).

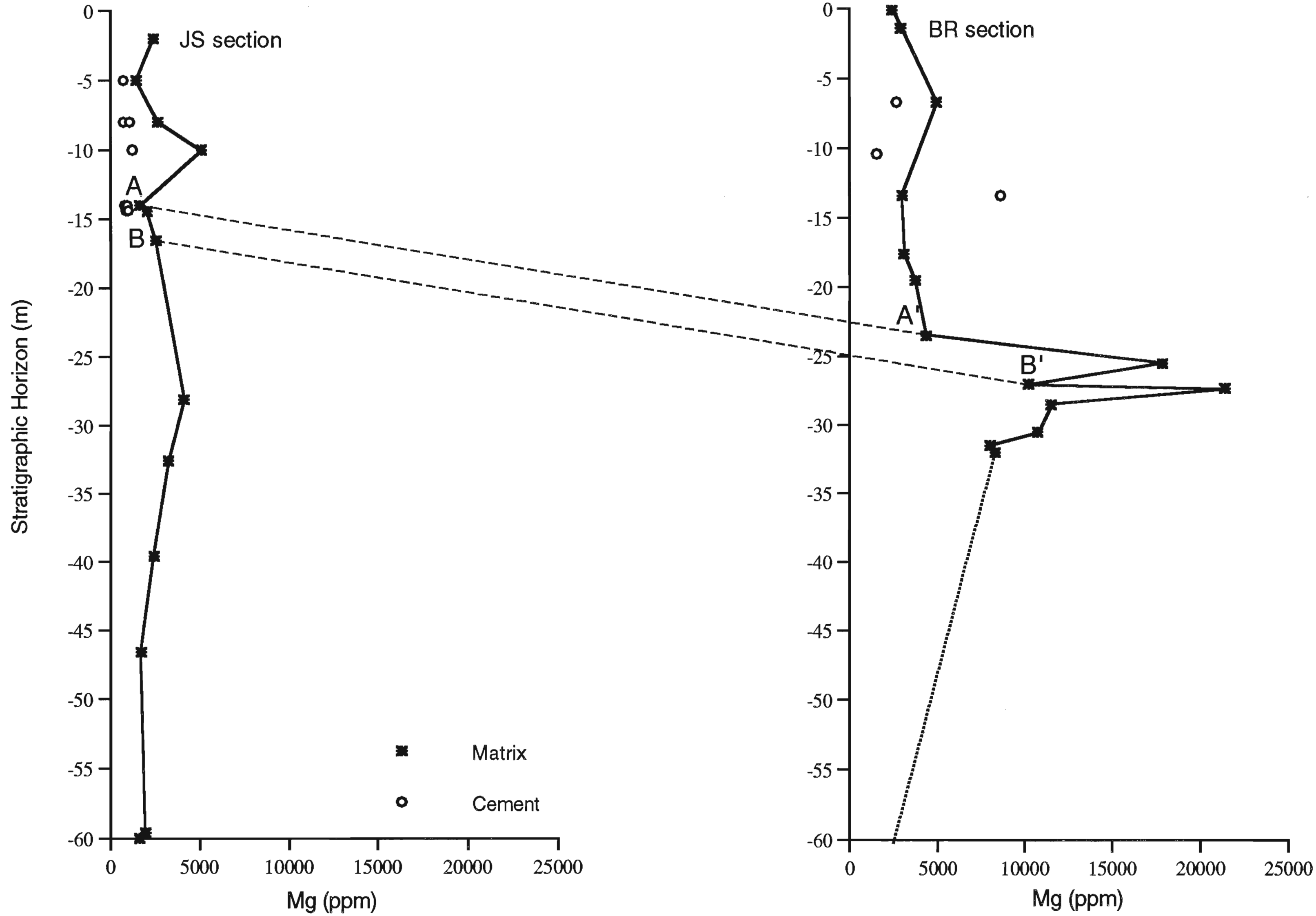


Fig.3-4 Stratigraphic comparison of matrix/cement from two sections, Madera Formation. A-A' and B-B' lines mark the upper and lower contact of the prominent limestone bed in the Jemez Springs Member.

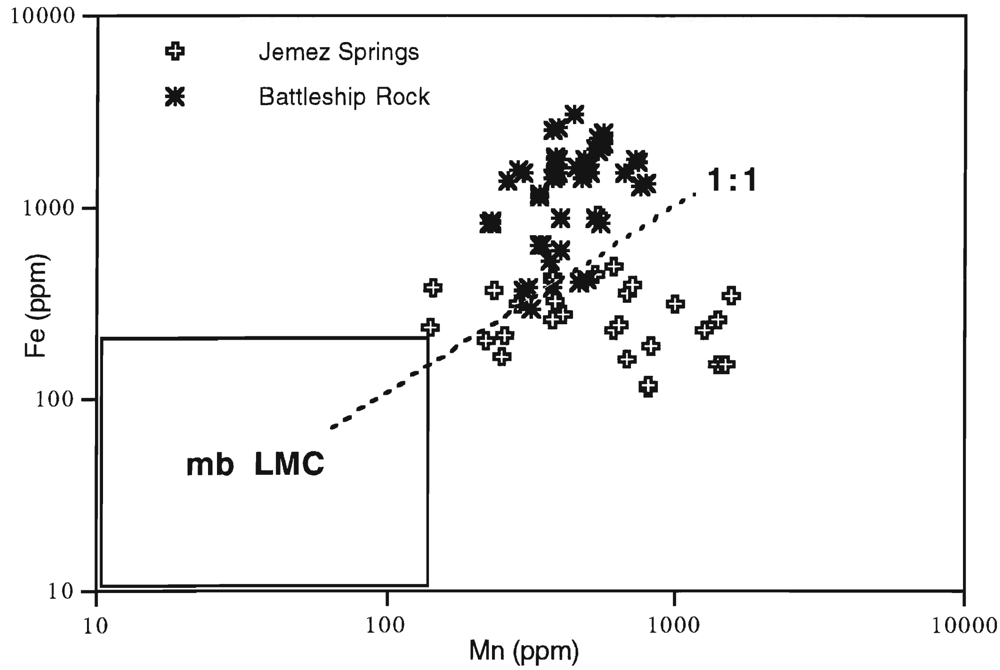


Fig. 3-5 Comparison diagram of matrix from two sections, Madera Formation. Modern brachiopod low-Mg calcite field is based on Brand & Veizer (1980)

It is generally agreed that Mn and Fe contents of carbonates are excellent indicators of both depositional (in unaltered specimens) and diagenetic (in altered specimens) processes (Brand, 1994). Specifically, Fe is an excellent proxy for redox (i.e., dysaerobic-aerobic water conditions) of the ambient fluid, whereas Mn serves as an indicator for both redox and continentality (cf. Broecker & Peng, 1982). As a redox indicator, Fe and Mn ratios vary in 1:1; whereas in its role of continentality proxy, Mn contents are greater than Fe by a ratio at least 2:1 (Brand & Logan, 1991). As such, It is postulated that the diagenetic fluid affecting the matrix at Jemez Springs had lower Sr and Fe contents but higher Mg and Mn contents than that operative in the Battleship Rock sequence. The vertical trends of Mn distribution in matrices between the two sections also suggest a greater degree of continentality for Jemez Springs (Fig. 3-6). This is true, in particular, for the upper part of the sequence. In all instances do the cements contain more Fe and Mn than the corresponding matrix (Fig. 3-6), further consistent with the postulated greater degree of diagenetic alteration of the cements than their coeval matrices.

Brachiopod

Evaluation of brachiopods from the Jemez Springs and Battleship Rock sections shows that about half of the studied population has Sr and Mn contents similar to those of mb LMC (Figs. 3-7, 3-8). Microstructural observations reveal that many specimens with Mn and Sr levels greater than those of mb LMC have retained the original texture of the calcite fibers within the secondary layer. Thus not all specimens that fall outside the Sr-Mn field for mb LMC are deemed altered, but, instead could reflect geochemical variation imparted by the depositional environment. Specimens deemed altered based on trace element criteria are listed in Table 3-2. It is also confirmed that the thicker Neospirifer shells are better preserved than those of either Composita or Linoproductus (cf. Figs. 3-7 & 3-8).

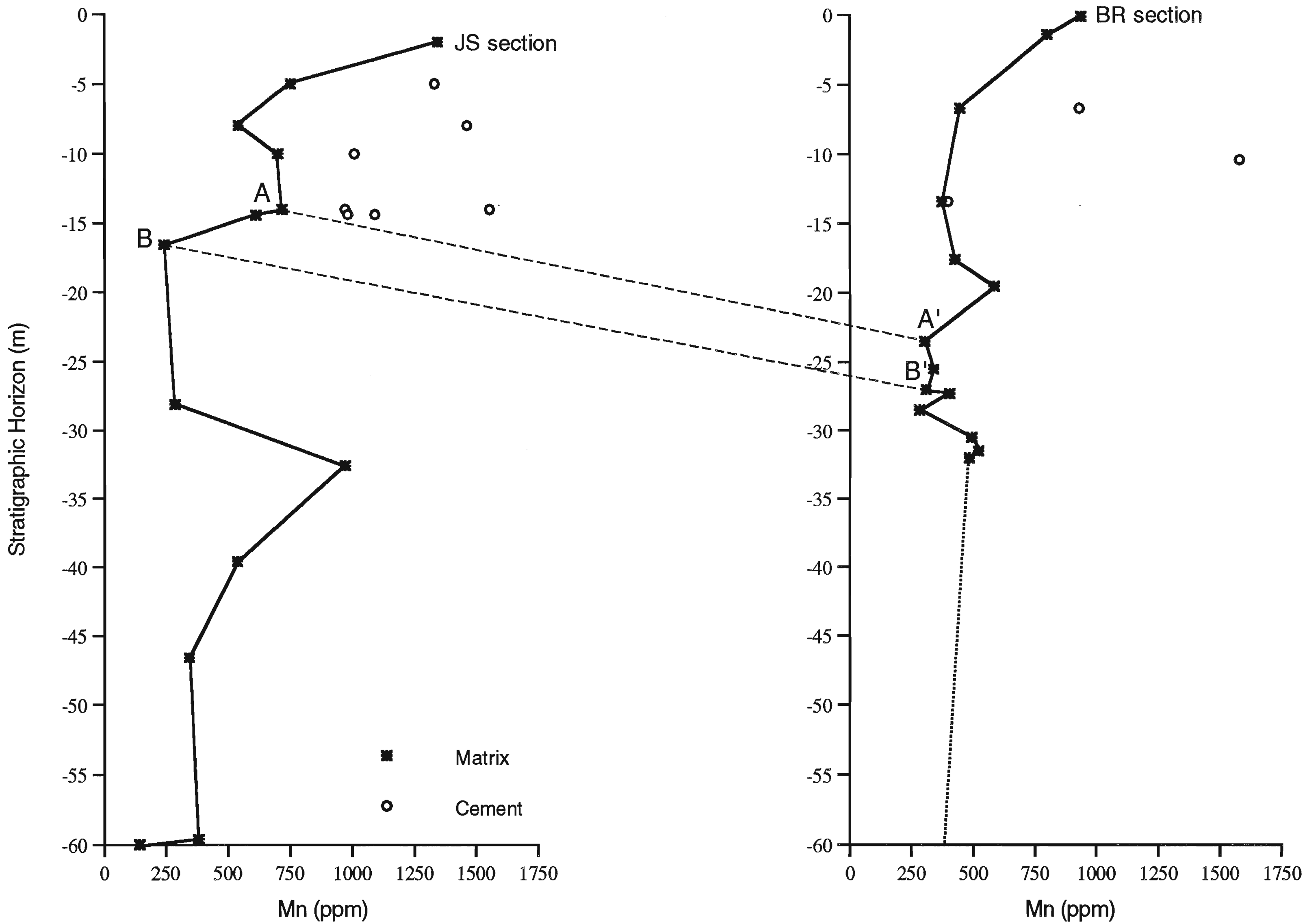


Fig. 3-6 Stratigraphic comparison of matrix/cement from two sections, Madera Formation. A-A' and B-B' lines represent the boundaries of the promonent limestone bed in the Jemez Springs Member.

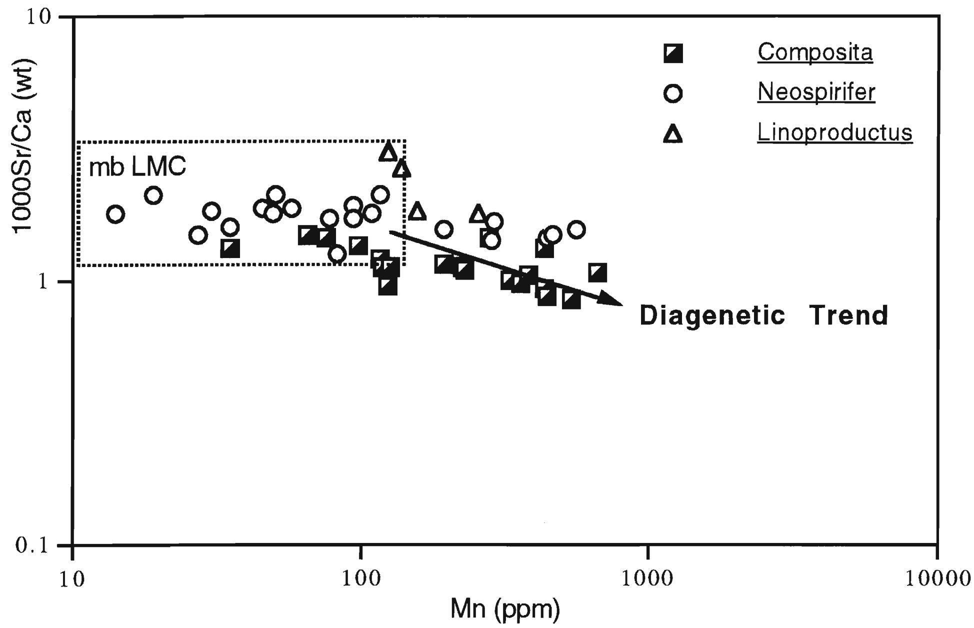


Fig. 3-7 Comparison of brachiopods from Jemez Springs. Modern brachiopod LMC field refers to Brand & Logan (1991).

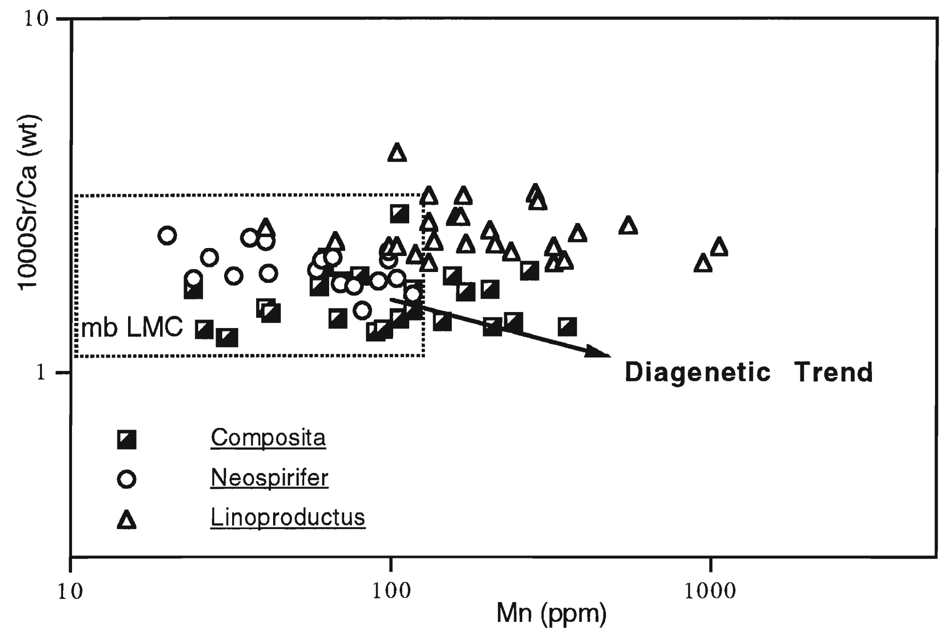


Fig. 3-8 Comparison of brachiopods from Battleship Rock. Modern brachiopod LMC field as in Fig. 3-7.

Table 3-2 Eliminated fossil samples of the Madera Formation by trace elemental criteria

#Sample	Fossil	1000Sr/Ca	Mg	Sr	Na	Fe	Mn
			(ppm)				
Jemez Springs							
UL-1A	Composita	0.88	2099	287	2129	358	364
UL-1B	Neospirifer	1.40	1299	423	1241	951	164
UL-2F	Neospirifer	0.97	1812	390	2850	263	1142
MMA-3	Neospirifer	1.01	2552	456	1122	152	273
MMA-4A	Linoproductus	1.25	1933	406	1538	47	75
MMA-4B	Linoproductus	1.14	1971	437	1584	45	80
MMA-12A	Brach. fragment	1.74	968	584	804	18	36
MMA-12B1	Brach. fragment	1.76	978	593	858	67	20
MMA-12B2	Brach. fragment	1.69	1056	587	904	174	22
UL-31	Composita	2.00	1515	593	1000	290	119
Battleship Rock							
BR-1	Composita	0.80	1802	264	62	172	
BR-2	Linoproductus	0.93	2055	298	258	259	732
BR-3	Brach. fragment	1.03	2658	421	86	556	651
BR-6	Brach. fragment	1.24	1385	372	554	80	58
BR-7	Brach. fragment	1.57	1093	527	765	45	35
BR-12	Neospirifer	2.36	4050	787	219	361	351
BR-34B	Linoproductus	3.09	7167	930	694	912	223
BR-37	Crinoid	4.07	4781	1157	181	364	424
BR-38	Composita	2.95	4020	957	797	615	174
BR-41B	Neospirifer	2.65	4060	900	930	620	129
BR-54	Neospirifer	2.26	4222	758	744	877	254
BR-58	Linoproductus	1.66	2377	502	622	280	82
BR-60	Bryozoan	2.36	5164	842	275	1040	515

Jemez Springs Composita have slightly lower Sr and Mg contents than their counterparts from Battleship Rock (Fig. 3-9). This may be a growth related phenomenon controlled by water temperature and nutrient contents at each depositional site (cf. Brand & Logan, 1991), and is further exemplified by their Fe and Mn contents (Fig. 3-10). Since altered specimens have been removed from the discussion, the observed Fe and Mn differences must be related to variations in depositional environments between the two localities. Thus, trace element data from brachiopods (Figs. 3-9 & 3-10) suggest that the Jemez Springs section was closer to shore during Madera time, seawater was more aerobic, and the water chemistry was more influenced by continental sources than the situation at Battleship Rock. In comparison with the stratigraphic analysis (e.g., Armstrong et al., 1979; Fig. 1-3), it is consistent with that the depositional environment of the Madera Formation was from shallow marine to near-shore marginal marine, and the Jemez Springs locality much closer to the Penasco Uplift than Battleship Rock.

Brachiopod-Matrix Comparison

In the absence of fossils for geochemical analysis, the researcher has no choice but rely on matrix geochemistry for both depositional (?) and diagenetic evaluation. Therefore, the presence of both constituents at Jemez Springs and Battleship Rock of the Madera Formation provides a good opportunity for comparing geochemical contents and trends. The comparison will concentrate on originally LMC brachiopods and aragonitic lime-mud now converted to diagenetic LMC micrite, microspar and pseudospar (Brand & Veizer, 1980).

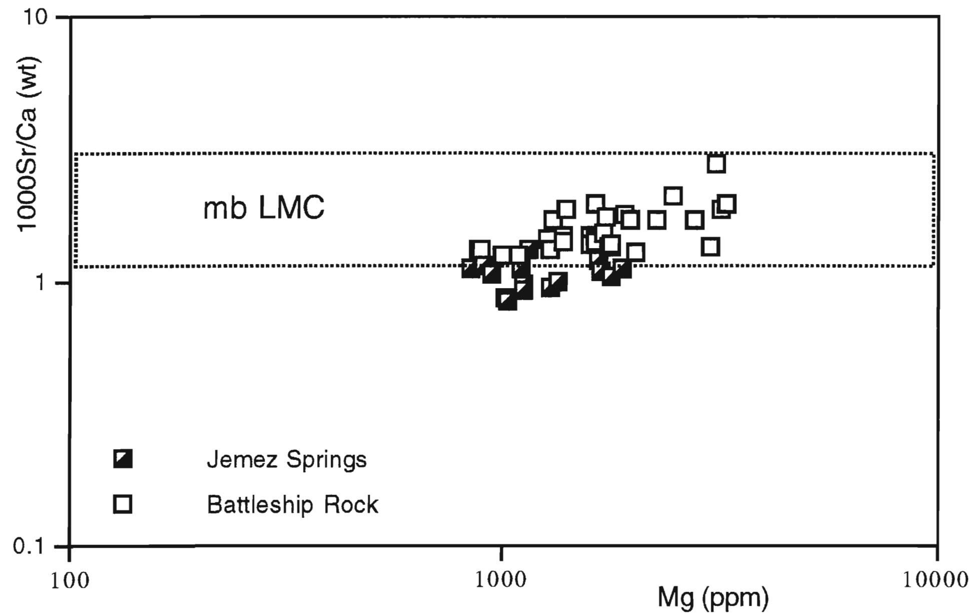


Fig. 3-9 Comparison diagram of Composita from the two sections, Madera Formation. The modern brachiopod LMC field is from Brand and Logan (1991).

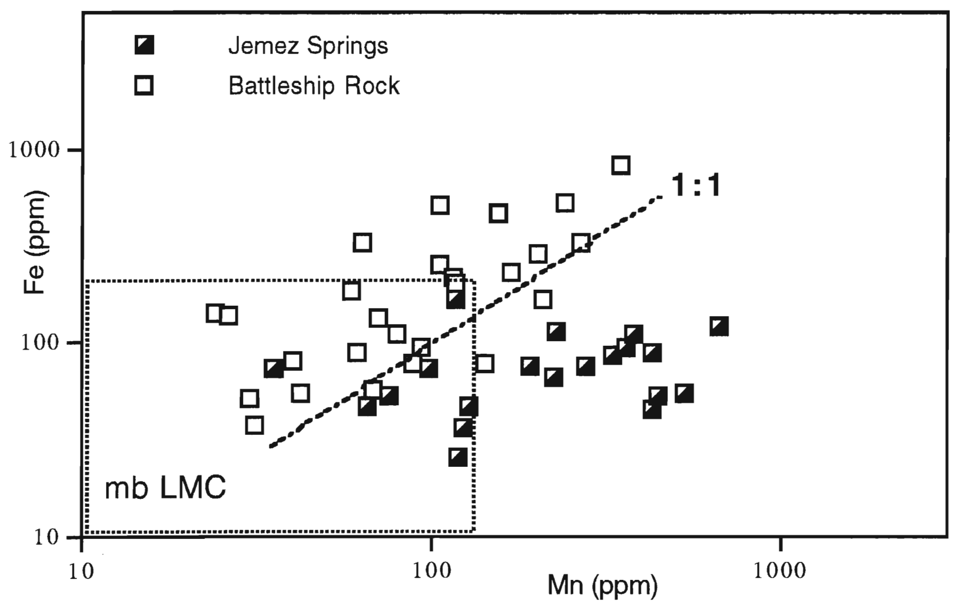


Fig. 3-10 Comparison diagram of Composita from two sections of the Madera Formation. The mbLMC field as in Fig. 3-9.

Jemez Springs brachiopod calcite contains in most cases more Sr than their coeval matrix (Fig. 3-11). This supports the assertion that Sr levels in matrix material are drastically changed from the original contents (Veizer & Demovic, 1974; Brand & Veizer, 1980; Brand, 1994). The difference in Sr contents and trends observed for Jemez Springs brachiopod-matrix also applies to the matched constituents from Battleship Rock (Fig. 3-11). Comparing with modern aragonite lime-mud (8,000-10,000 ppm Sr, Milliman, 1974), the decrease in Sr contents in matrix material by a factor of 10 to 25, suggests that Sr in micrite and associated material is rarely preserved at depositional levels.

The mean Sr levels in brachiopods from Jemez Springs are relatively constant at about 500 ppm, with some variation around the ledge-forming limestone bed (B; Fig. 3-11). In contrast, the mean Sr levels in brachiopods from Battleship Rock increase from about 600 ppm to 900 ppm at the base of the ledge-forming limestone bed (B'; Fig. 3-11). The distinct change in Sr contents at the limestone beds corresponds to the lower boundary of the Jemez Springs Member (cf. Fig. 1-2).

Interestingly, the Sr trends exhibited in brachiopods is mimicked by their Mg contents, and the matrix contains more Mg than their coeval brachiopods (Fig. 3-12). This agrees well with post-depositional diagenetic processes and results observed in originally aragonitic lime-mud converted to micritic matrix (cf. Brand & Veizer, 1980). The anomalous high Mg level (17, 857 ppm) encountered in Figure 3-12 (the Battleship Rock section), is probably related to dolomitization of the matrix.

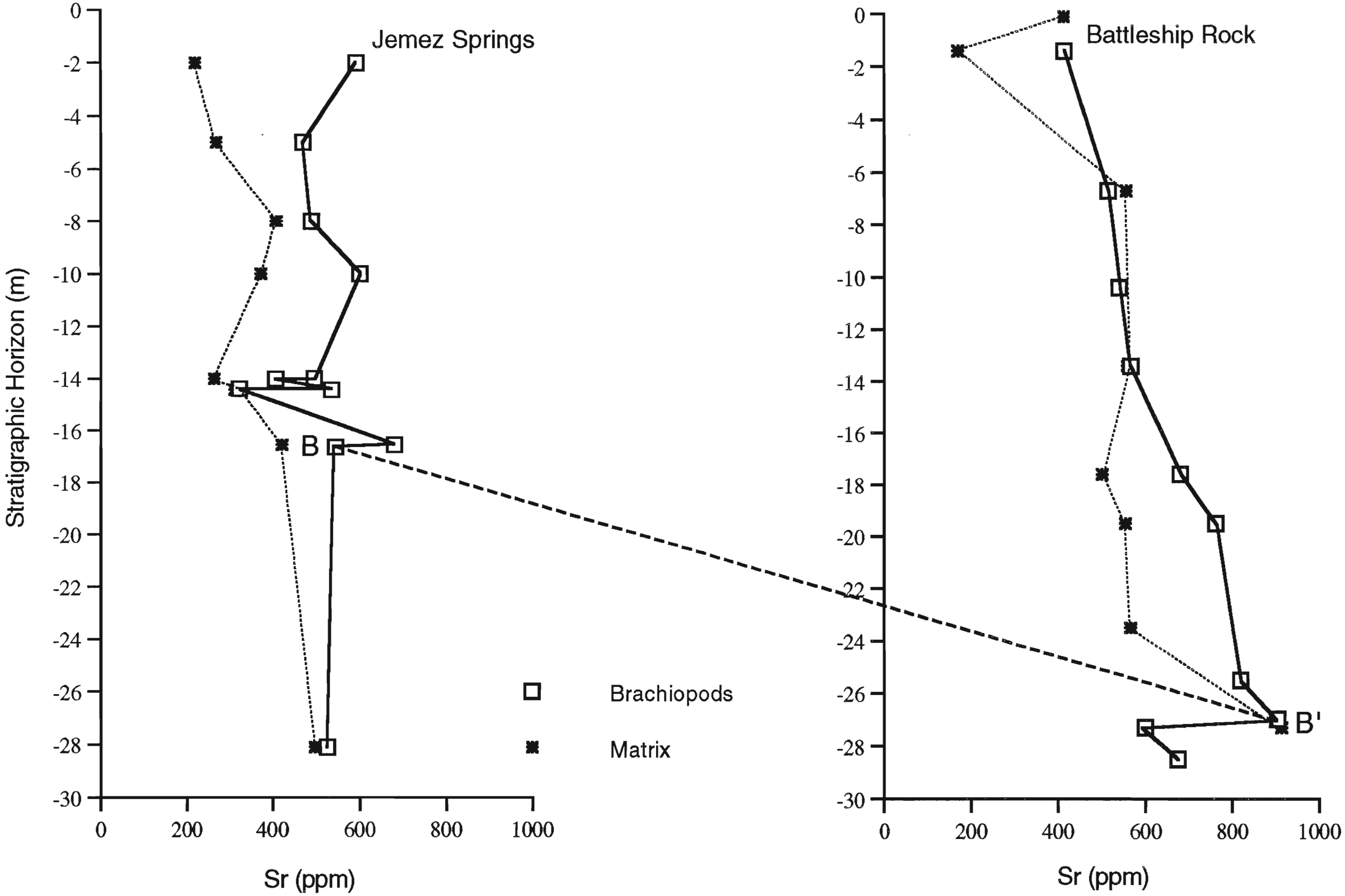


Fig. 3-11 Stratigraphic comparison of mean Sr variation between two sections, Upper Madera Formation

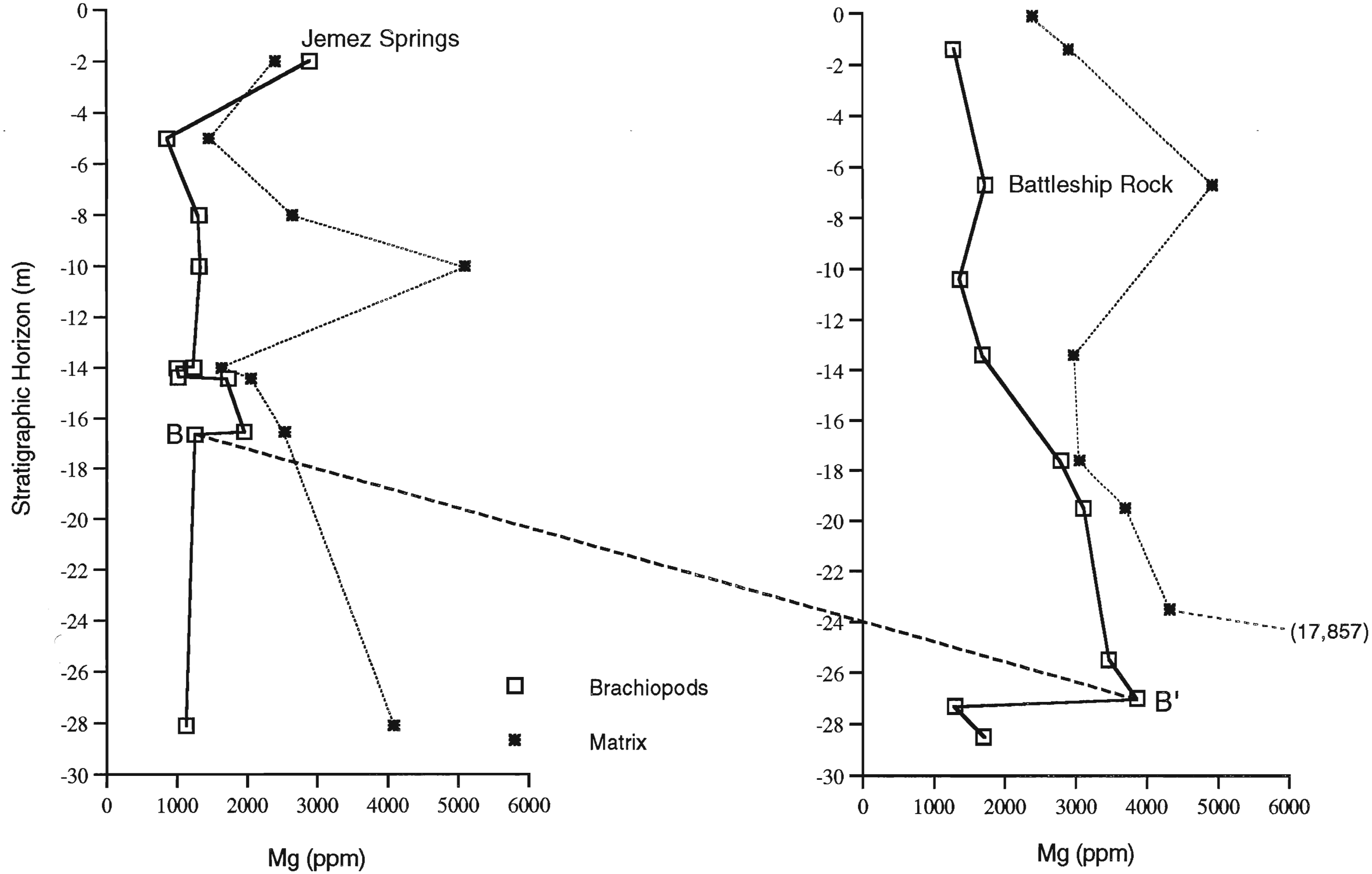


Fig. 3-12 Stratigraphic comparison of mean Mg variation between two sections, Upper Madera Formation

Unlike the similarity between Sr and Mg trends for both brachiopods and matrix, divergent and/or invariant trends are shown for Mn and Fe (Figs. 3-13, 3-14). The Mn trends between the two sections may be a depositional feature related to their offshore positions in the Penasco Uplift area. However, the Fe content in the Madera brachiopods is relatively low with less than 500 ppm, whereas the matrix is as high as 2,707 ppm (Fig. 3-14). The Mn and Fe contents in coeval matrices are so higher than those observed in modern lime-mud sediments (e.g., Milliman, 1974; Bathurst, 1976; Brand & Veizer, 1980), suggesting that the originally aragonitic matrix was extensively altered by post-depositional processes, while a majority of brachiopods retained their original morphology, mineralogy and trace elemental geochemistry.

In summary, the comparison between brachiopods and matrices has demonstrated that matrix carbonate is altered, but that the degree of alteration is variable throughout the stratigraphic section. Moreover, the diagenetic overprinting is in all cases neither uniform and/or constant, nor geochemically destructive. Care must be taken when using matrix to infer depositional parameters from its chemical compositions.

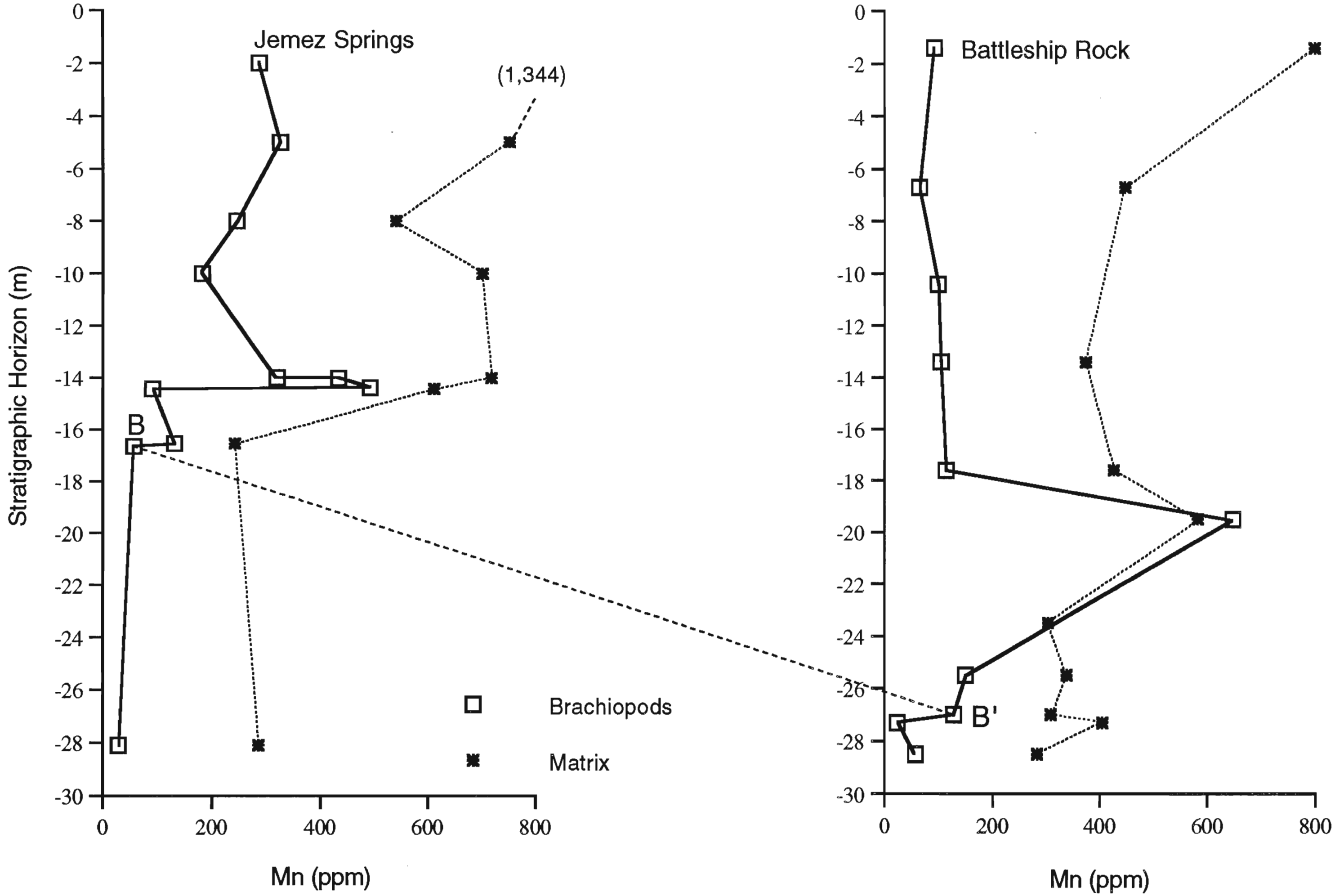


Fig. 3-13 Stratigraphic comparison of mean Mn variation between two sections, Upper Madera Formation

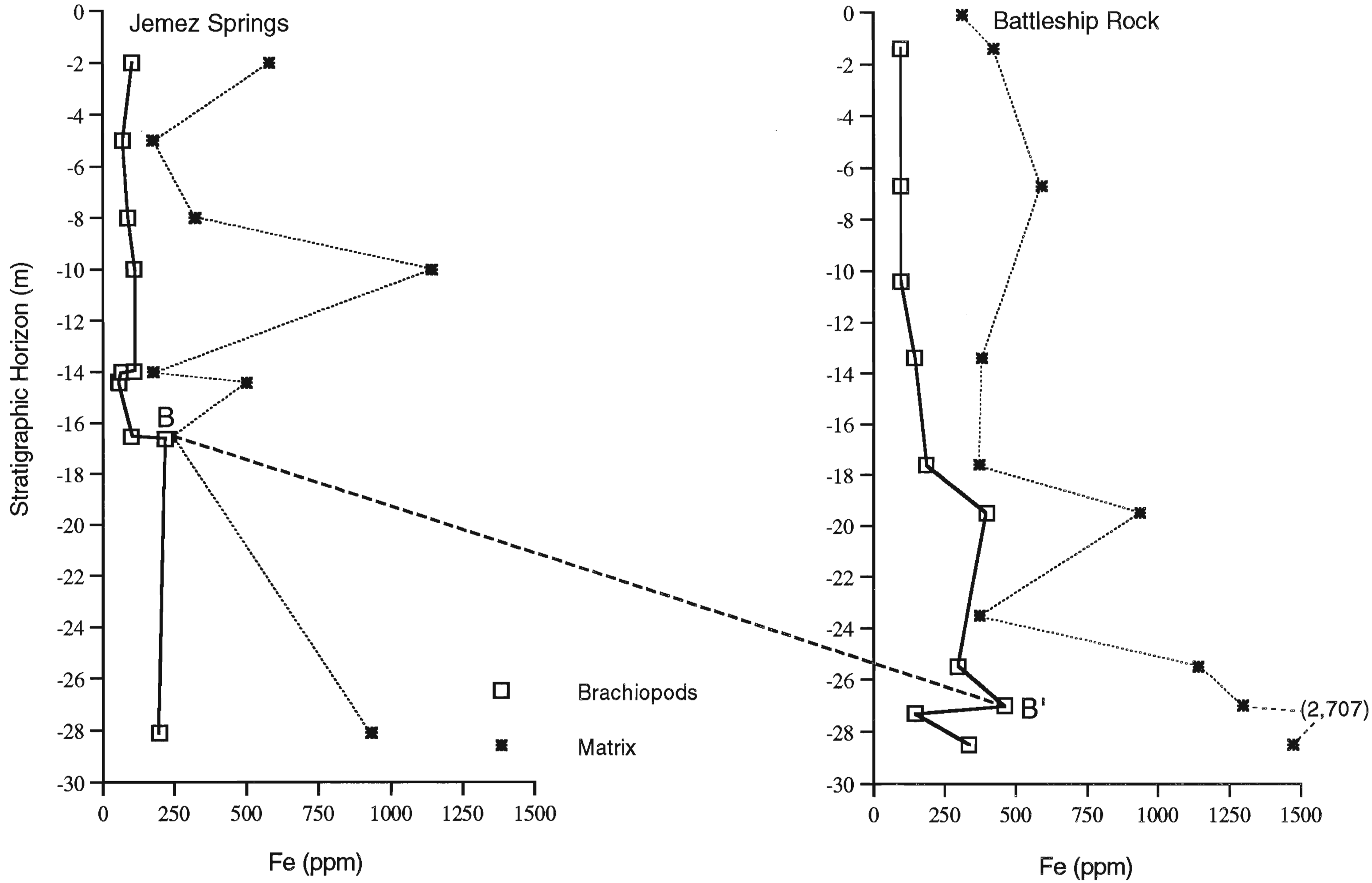


Fig. 3-14 Stratigraphic comparison of mean Fe variation between two sections, Upper Madera Formation

PETROGRAPHIC ANALYSIS

Thin sections were prepared for the upper part of the Jemez Springs and Battleship Rock sections. Specimens were cut to a thickness of 30μm, and prior to covering were stained according to the method prescribed by Lindholm and Finkelman (1972). In general, staining allows for the identification of dolomite and semiquantitative determination of Fe in the carbonate minerals.

Petrographic analysis of the sediments in the upper part of both sections provides supporting evidence for the geochemical interpretation. Allochems such as brachiopods, crinoids, corals, algae and forams are recognized (Table 3-3). Relative abundance of matrix, cements, dolomite, quartz and iron minerals is noted. Diagenetic features such as stylolitization and silicification are also noted in the specimens.

Fossil allochems are abundant in the upper part of the Jemez Springs section (Table 3-3), dominated by a brachiopod-bryozoan-crinoid assemblage. Detrital quartz is most common in the uppermost part of the section (Fig. 3-15 A; Table 3-3), but decreases with the increasing depth. Sparite cement is present, especially within brachiopod valves (Fig. 3-15B). Microspar is common (Fig. 3-15C), with a high micrite concentration at horizon of 39.6 m (Fig. 3-15E). Vein sparite cement is also noted in the lowest part of the Jemez Springs section (Fig. 3-15F).

Alteration of the primary layers in brachiopods is found in thin section UL-7 (Fig. 3-15D), which clearly shows the "destruction" of the primary prisms by diagenesis. In addition, dolomite is essentially absent in the rocks from

Component / Sample No.	Brachiopod	Bryozoan	Crinoid	Coral	Alga	Foraminifera	Peloid	Micrite	Sparite	Microspar	Pseudospar	Stylolite	Dolomite	Quartz: Detrital	Quartz: Silicification	Iron mineral
JS section																
UL-6	xxx	x			x				xx	xx	x			xxx	x	xx
MMA-255	xx	xxx	xx	x					x	xx	x	x		x	x	x
MMA-265	xx	xxx	xx	x	x				x	xx					xxx	x
UL-7	xx	xx	xx	x					x	xxx					x	x
UL-9							xx	xxx	x		xx	x		x	x	x
UL-13	x		x					x	x	xxx	x			x		x
BR section																
BR-3	x	xx	x		x	x		x	x	xxx	x				x	x
BR-8	x	x			x		x	xxx	x	x	x	xx		x		
BR-9	xx	xxx	xx	xx	x	x		xx	xx			x	x			
BR-10	xx	xxx	x	x		x		xx	x	x			xx		x	x
BR-11	xxx	xxx	x	x		x		x	x			x	xxx		x	
BR-16	xx	xx	xx	x	x			x	x	xx				x		

Table 3-3 Summary of petrographic analysis from the Jemez Springs and Battleship Rock sections, Madera Formation. Key for symbol: x-present; xx-common; xxx-abundant.

Fig. 3-15 Photographs of stained thin sections from the Jemez Springs section, Madera Formation, New Mexico.

A: Sample UL-6; -10m; detrital quartz grains; 32x, PPL;

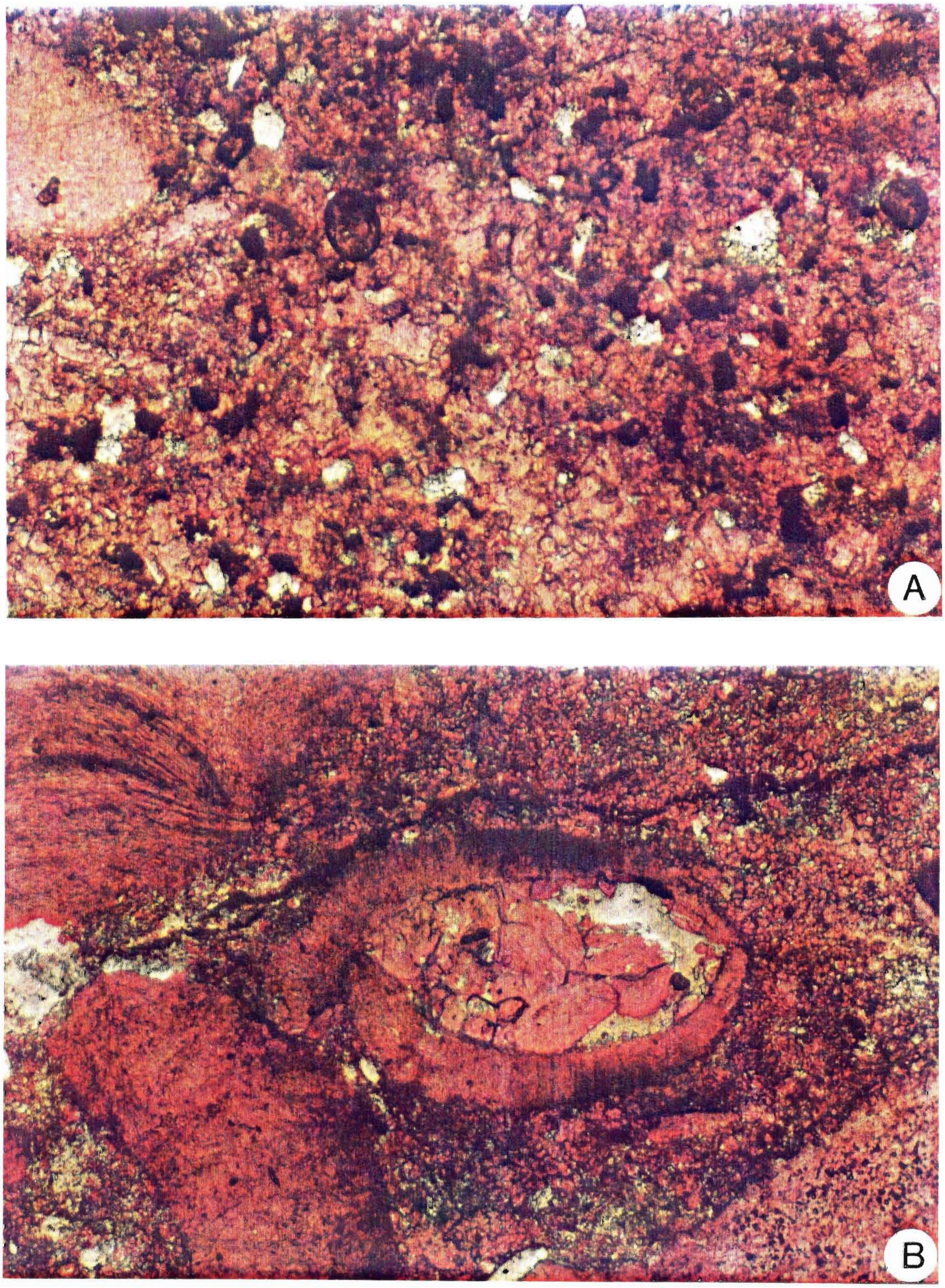
B: Sample MMA-255; -16.55m; sparite within a brachiopod; 32x, PPL;

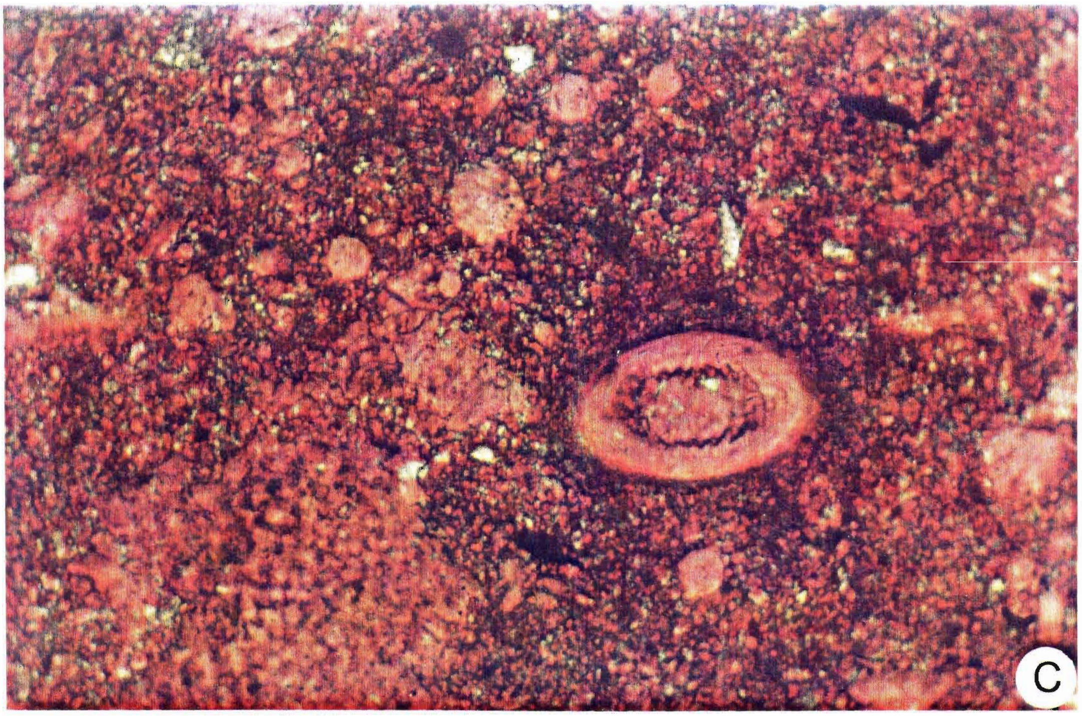
C: Sample UL-7; -28.1m; microspar, 32x, PPL;

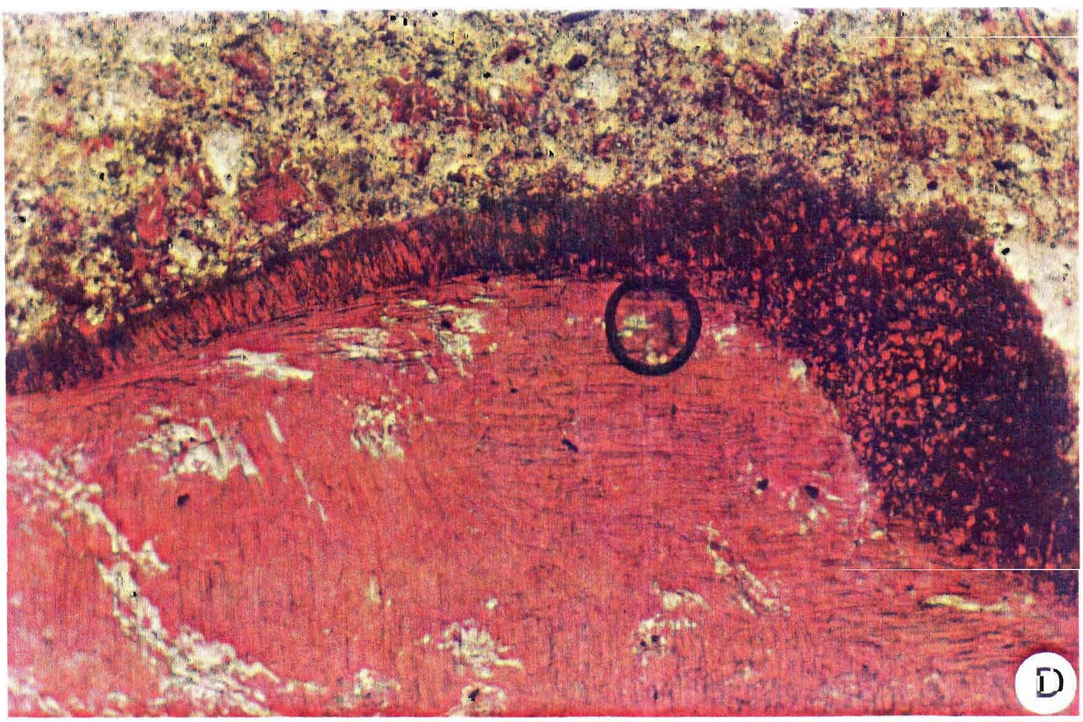
D: Sample UL-7; -28.1m; primary and secondary layers of brachiopod shell structures; 32x, PPL;

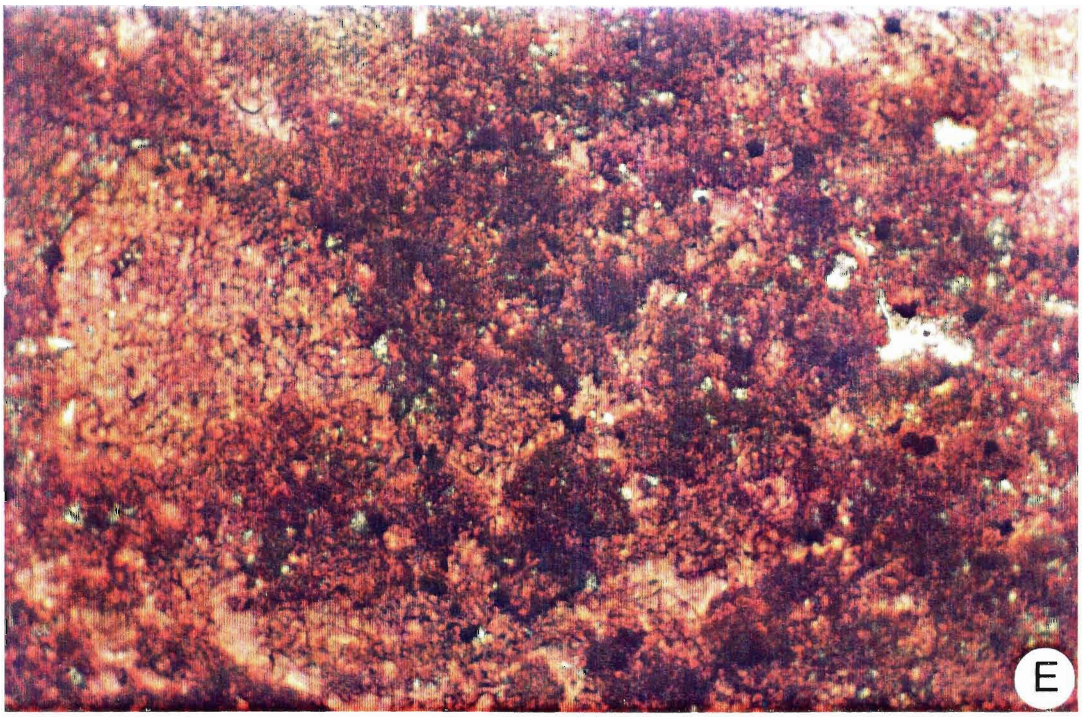
E: Sample UL-9; -39.6m; micrite, peloid and iron minerals; 32x, PPL;

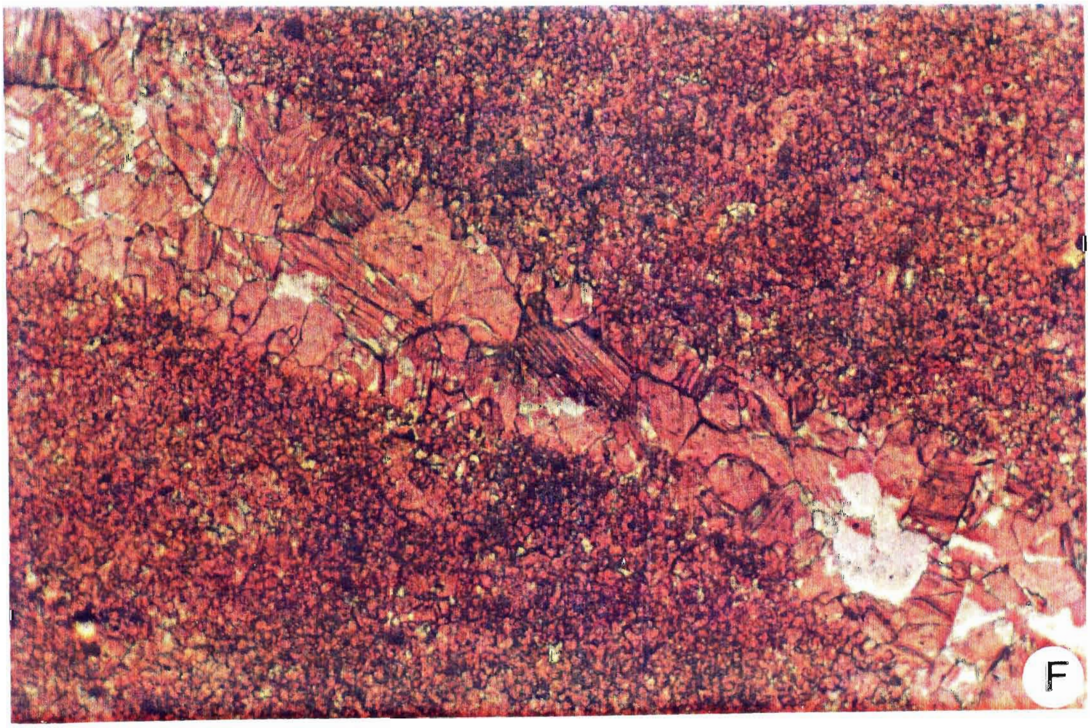
F: Sample UL-13; -60m; microspar and sparite; 32x, PPL.


A
B


C


D


E


F

Jemez Springs (Table 3-3). The upward increase of detrital quartz, in combination with the Mn data, may suggest an upward shallowing sequence and/or continental encroachment. The source of detrital quartz was apparently from the Penasco Uplift (cf. Fig. 1-3).

Samples at Battleship Rock share some features with those at Jemez Springs such as the fossil assemblage (Table 3-3). However, detrital quartz, peloids and iron minerals are sparse (Fig. 3-16A, E, and F). Other textural features such as stylolites are common (Fig. 3-16B), and dolomite is most common in BR-11 and diminishes upward in the sequence (Fig. 3-16C). Silicification, which was more common throughout the Jemez Springs section, is spotty in the sediments at Battleship Rock (Fig. 3-16D).

The Battleship Rock section is also different in its dolomite content and distribution (Table 3-3). Samples at both localities with less than 5,000 ppm Mg contain few to no dolomite (Fig. 3-12), whereas samples characterized by higher Mg contents (>6,000 ppm) show significant amount of dolomite (Fig. 3-16C). Thus, Mg content of matrix is a good elemental indicator of dolomitization.

Overall, petrographic observations concur with the conclusions drawn from trace element data. The Jemez Springs section is nearer to the Penasco Uplift which was the source of detrital quartz, and a greater dolomitization occurred at Battleship Rock.

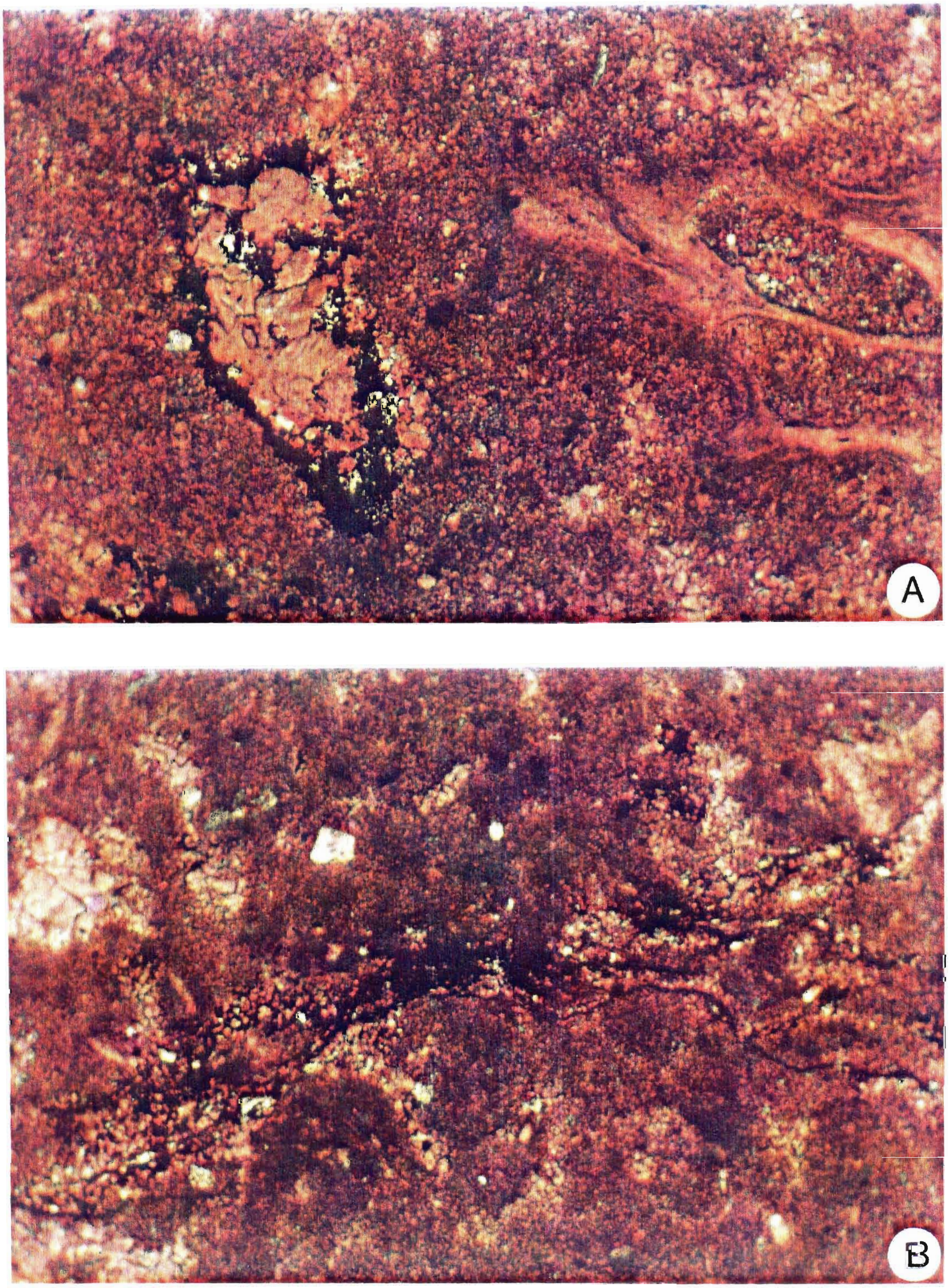
Fig. 3-16 Photographs of stained thin sections from the Battleship Rock section, Madera Formation, New Mexico.

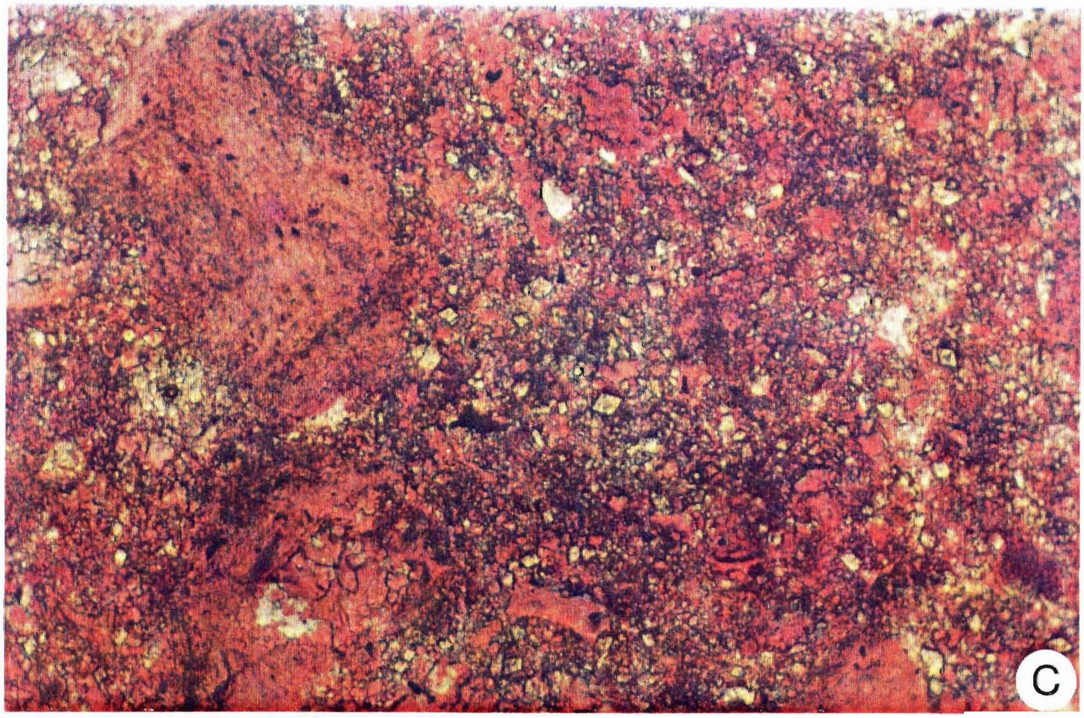
A: Sample BR-3; -6.7m; microspar and iron minerals; 32x, PPL;

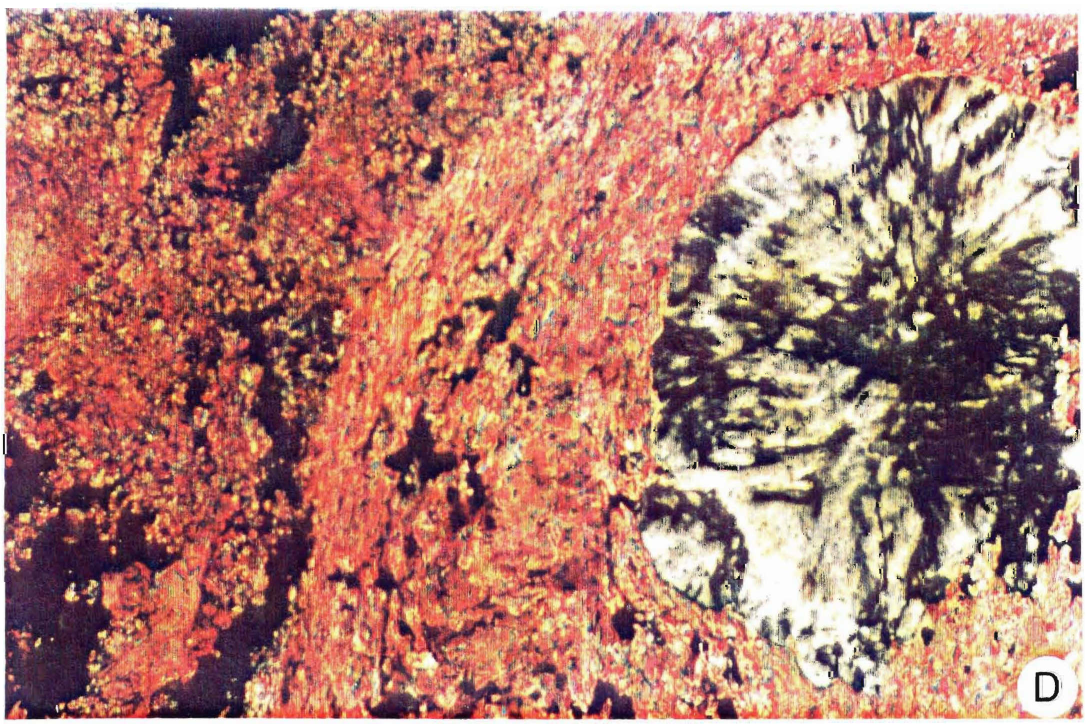
B: Sample BR-8; -23.5m; micrite and stylolite porosity; 32x, PPL;

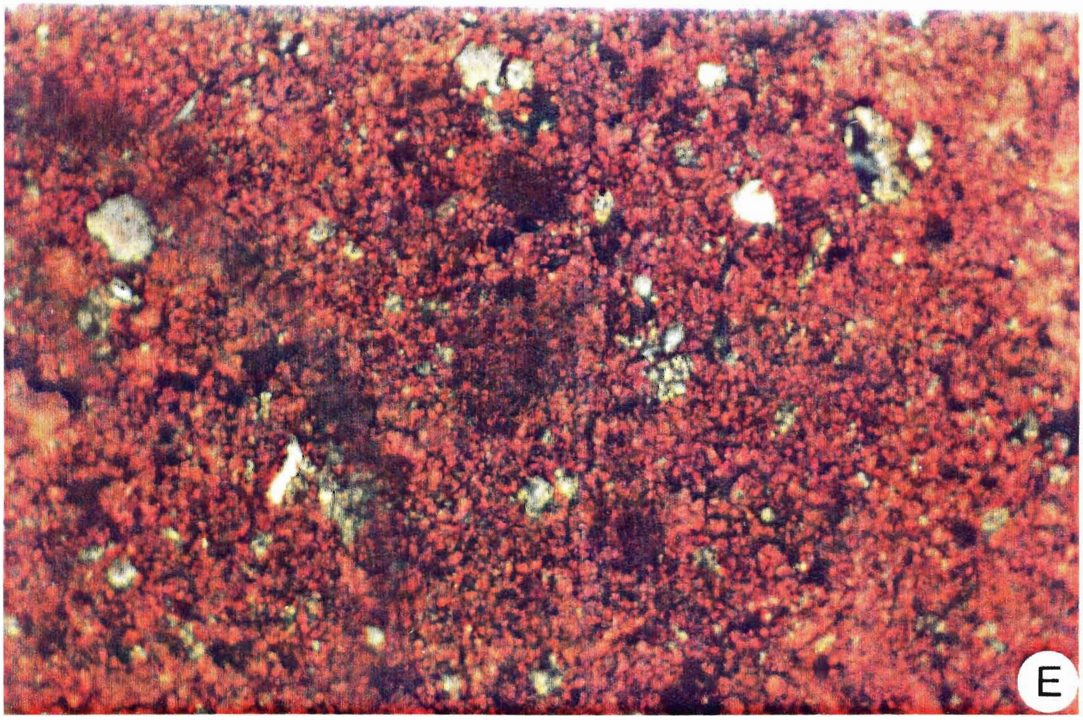
C: Sample BR-11; -27.3m; rhombohedral dolomite grains; 32x, PPL;
D: Sample BR-11; -27.3m; silicification; 32x, XPL;

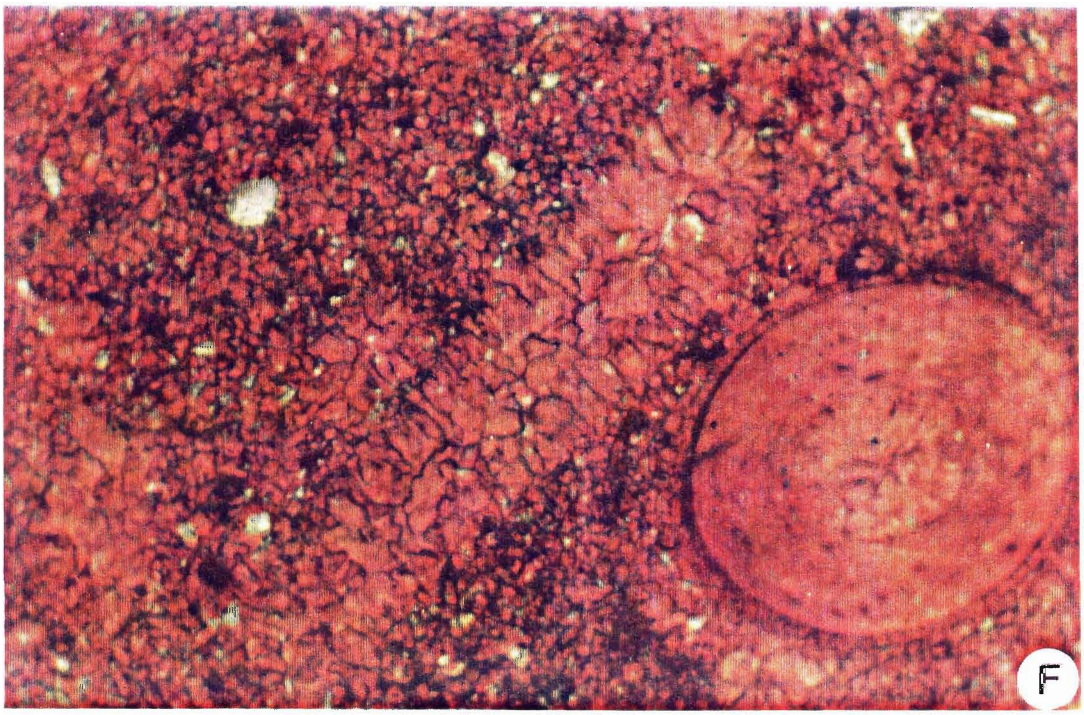
E: Sample BR-16; -31.5m; detrital quartz grains; 32x, XPL;
F: Sample BR-16; -31.5m; algal tube, microspar and brachiopod spine; 32x, PPL.


A
B






E


F

SUMMARY

Trace elemental examination and comparison of different carbonate constituents from the Madera Formation show that cements and matrix have undergone drastic post-depositional alteration relative to their corresponding brachiopods. Two or more source fluids are probably responsible for the diagenetic trends. As for the depositional environment, Jemez Springs is closer to the Penasco Uplift; seawater is more aerobic, and the water chemistry is more influenced by continental sources than those at Battleship Rock. Furthermore, stronger dolomitization is also the character of the Battleship Rock section.

Chapter 4

ISOTOPE GEOCHEMISTRY OF BRACHIOPODS FROM THE MADERA FORMATION

INTRODUCTION

The application of stable isotopes to carbonate geology has dramatically expanded since Harold Urey's initial work (cf. Urey, 1947; Hecht, 1985; Faure, 1991). About 300 stable isotopes are recognized in nature, and some of the properties of carbon and oxygen isotopes are listed in Table 4-1.

Table 4-1 C and O isotopes used in this research (Arthur et al., 1983)

Element	Isotope	Relative abundance (%)	Natural abundance variation (‰)
C	^{12}C	98.894	$^{13}C/^{12}C=110$
	^{13}C	1.106	
O	^{16}O	99.762	$^{18}O/^{16}O=100$
	^{17}O	0.038	
	^{18}O	0.200	

Basically, oxygen (and carbon) isotope incorporation into carbonate minerals is governed by the fractionation factor α:

$$\alpha_{S\text{-}L} = R_S / R_L \qquad (4\text{-}1)$$

where R is the isotopic ratio of the sample ($^{18}O/^{16}O$), and S and L represent the solid and liquid phase, respectively. For any given system, α is temperature dependent and approaches unity as temperature increases (Faure, 1986).

The oxygen isotopic composition of a sample is usually expressed as per mil (‰) relative to a standard called SMOW (Standard Mean Ocean Water, cf. Craig, 1961):

$$\delta^{18}O = [\ (^{18}O / ^{16}O)_{Samp} / (^{18}O / ^{16}O)_{SMOW} - 1\ ] * 1000 \qquad (4\text{-}2)$$

Consequently, a positive value of $\delta^{18}O$ indicates enrichment of a sample in ^{18}O compared to SMOW, whereas a negative value implies depletion of ^{18}O in the sample. The $\delta^{18}O$ value of sea water is close to 0‰ and varies only within narrow limits. Because of the existence of three stable isotopes of oxygen and two stable isotopes of hydrogen (cf. Table 4-1), normal water molecules have nine different isotopic configurations (Faure, 1986). Thus, the evaporation of sea water results in isotopic fractionation of oxygen so that ^{16}O preferentially enters the vapor, while ^{18}O is concentrated in the liquid phase.

The isotope composition of oxygen in carbonate samples is given in per mil (‰) relative to the PDB standard based on the Cretaceous belemnites of the Peedee Formation in South Carolina. Since both SMOW and PDB have been used to express the isotopic composition of oxygen, the conversion of resulting δ values was given as (Friedman & O'Neil, 1977):

$$\delta^{18}O_{SMOW} = 1.03086\ \delta^{18}O_{PDB} + 30.86 \qquad (4\text{-}3)$$

The precision of $\delta^{18}O$ values is of the order of about 0.2‰, or better (Faure, 1986).

Although the discussion above focused on oxygen isotopes, the same principles are also applicable to carbon (cf. Veizer, 1983). Generally, biological carbon compounds are greatly enriched in the light isotopes (^{12}C), whereas the heavy ones (^{13}C) are retained in carbonate or carbon dioxide. In general, $^{13}C/^{12}C$ ratios of biogenic substances result from both thermodynamic and kinetic fractionations, but most biological carbon isotope fractionations are due to kinetic rather than equilibrium effects (Schidlowski, 1986).

It is normally accepted that both $\delta^{18}O$ and $\delta^{13}C$ are effective tracers in carbonate geochemistry, and can provide unique information on the degree of diagenetic alteration of fossil shells and skeletons (cf. Veizer, 1983; Brand, 1987; O'Neil, 1987). However, successful application of these isotopes depends not only on how precisely the isotopic data are measured in the laboratory, but also on how well the isotopic data are integrated with other information, such as trace elements and shell microstructures. A basic requirement for isotopic study is the utilization of "least-altered" or, better still preserved LMC specimens (e.g., Brand & Veizer, 1981; Popp et al., 1986; Adlis et al., 1988; Brand, 1989; Bates & Brand, 1991). Recent investigations have even shown that sample material and type (e.g., fossil shells, cements and matrix) can affect the diagenetic interpretation and variation of isotopic trends (Brand, 1994).

SAMPLE PREPARATION

Approximately 5-10 mg of powdered sample was reacted with 100% phosphoric acid at 50°C for 30-45 minutes (cf. McCrea, 1950; Brand, 1982). Then, on a line of cold traps monitored by an Edwards Thermocouple-507, purified CO_2 gas was trapped and sealed in break seals for isotope (C, O) analyses. In all, 103 samples were measured on a V.G. Micromass® 602D Mass Spectrometer at the Stable Isotope Laboratory, Ottawa-Carleton Geoscience Centre. The isotopic ratios are reported in the standard notation (δ) relative to PDB in permil (‰). The average accuracy and reproducibility compared to N.B.S. No.19 (TS Limestone) are better than 0.2‰, with all data being corrected for ^{17}O (cf. Craig, 1957).

DIAGENETIC TREND

103 specimens were analyzed and their isotope data are reported in Appendix II. These specimens include fossil shells (brachiopods and crinoids), cements and matrices. The $\delta^{18}O$ values of the Madera Formation allochems range from -9.2 to -2.9‰, with a mean of -4.8 ± 0.10‰; whereas the $\delta^{13}C$ values range from -5.1 to +4.2‰, with an average of +0.4 ± 0.25‰. Specifically, the data from Jemez Springs have a lower $\delta^{18}O$ range from -6.6 to -3.4‰, and a higher $\delta^{13}C$ range from -5.1 to +3.8‰; whereas the $\delta^{18}O$ and $\delta^{13}C$ values of Battleship Rock range from -9.2 to -2.9‰ and -4.5 to 4.2‰, respectively.

Brand (1981) found that brachiopods from the Lower Pennsylvanian Kendrick Shale of eastern Kentucky had lower $\delta^{18}O$ compositions of -5.1 to

-4.1‰, and +1.2 to +2.3 ‰ for $\delta^{13}C$ (N = 6). Veizer et al. (1986) reported an average $\delta^{18}O$ value of -4.5 ± 1.5‰ for Carboniferous brachiopods from North America (N = 37). Adlis et al. (1988) analyzed two Upper Pennsylvanian sections in north Texas, the Necessity Shale and Colony Creek Shale, and reported $\delta^{18}O$ values ranging from -4.2 to -0.1‰ and $\delta^{13}C$ from -1.1 to +4.2‰ for the fibrous layers in brachiopods (N = 95). More recently, Grossman et al. (1993) took brachiopod samples from the uppermost Jemez Springs section, and reported $\delta^{18}O$ values ranging from -4.5 to -2.1‰, and $\delta^{13}C$ values from +2.2 to +4.8‰ (N = 87). Compared with these studies, our isotopic data are relatively depleted in $\delta^{18}O$ and $\delta^{13}C$, implying a higher degree of diagenetic alteration. If we focus on the Madera brachiopod shells only (N = 72), our $\delta^{18}O$ and $\delta^{13}C$ values are narrowed to -5.6 to -2.9‰ and -2.4 to +4.2‰, which are much closer to Brand's (1981) and Grossman et al.'s (1993) data.

To assess the effect of diagenesis, matrix and cement samples were analyzed for oxygen and carbon, and in most instances these contain lighter $\delta^{18}O$ values than the preserved brachiopod specimens. Their lighter $\delta^{13}C$ values further confirm the pervasive alteration of matrices and cements, and the general preservation of the selected Madera brachiopods (Figs. 4-1, 4-2). Reviewing the initial evaluation involving trace elemental and microstructural evidence, about 21 brachiopods of 132 were deemed altered and removed from the data base. Isotope evaluation shows that an additional 7 specimens have anomalous values (Table 4-2). This may be due to diagenetic alteration, sample preparation or analytical effects, and the exact cause is difficult to ascertain. Obviously, these specimens should be deleted from the following discussion on depositional aspects.

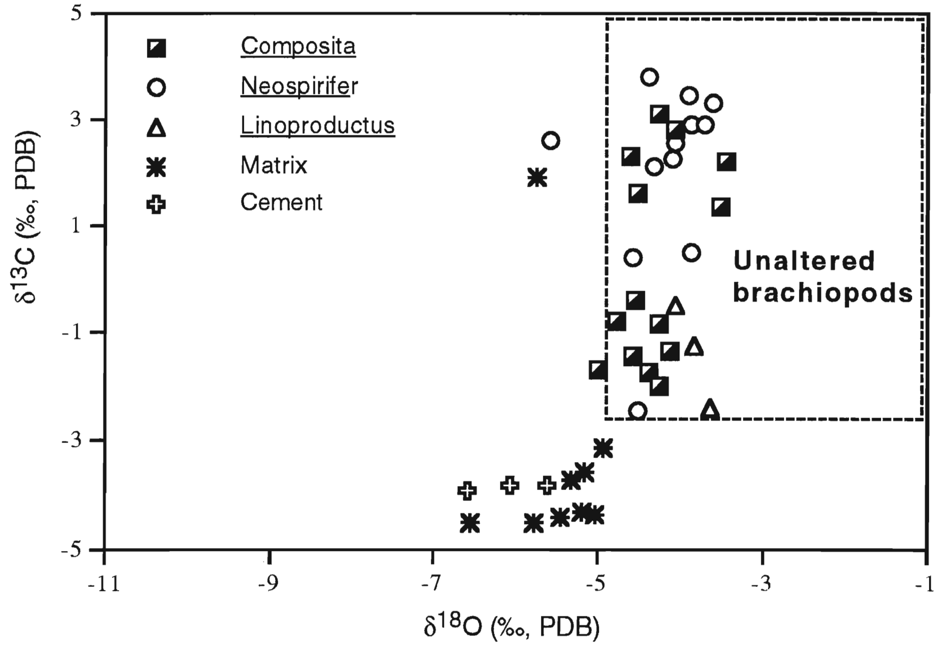


Fig. 4-1 Scatter diagram of $\delta^{13}C$ vs $\delta^{18}O$ for samples from the Jemez Springs section.

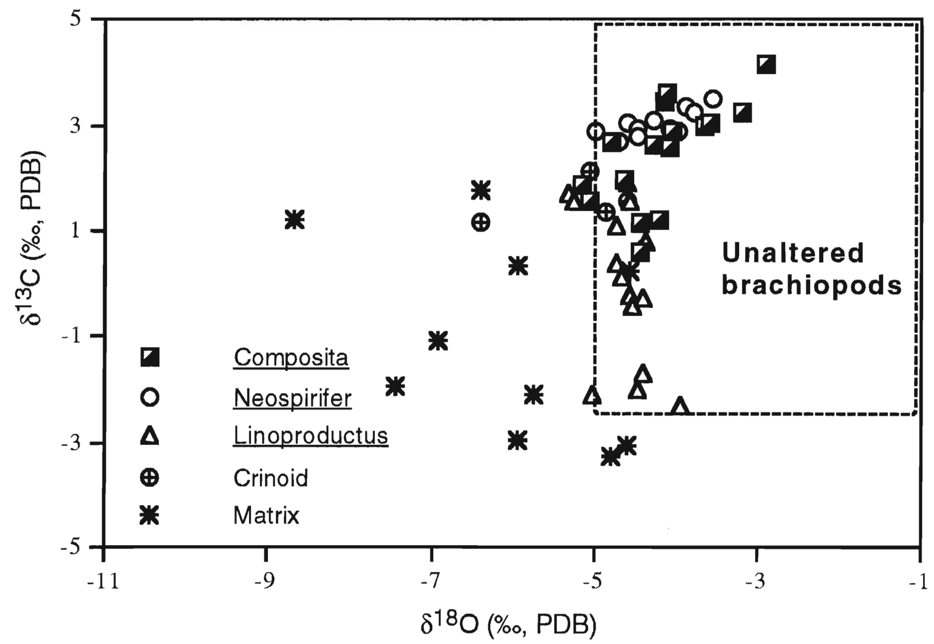


Fig. 4-2 Scatter diagram of $\delta^{13}C$ vs $\delta^{18}O$ for samples from Battleship Rock.

Table 4-2 Eliminated fossil samples of the Madera Formation based on isotopic criteria

#Sample	Fossil	$\delta^{18}O$	$\delta^{13}C$	Mg	Sr	Na	Fe	Mn
		‰		(ppm)				
Jemez Springs								
UL-34A	Neospirifer	-5.59	2.60	1574	724	892	523	116
Battleship Rock								
BR-31	Linoproductus	-5.04	-2.11	2088	758	450	216	170
BR-42	Linoproductus	-5.33	1.69	3296	801	1129	642	212
BR-45	Composita	-5.06	1.55	3082	769	1037	509	105
BR-46B	Neospirifer	-5.00	2.88	2277	755	1055	380	65
BR-55B	Linoproductus	-5.26	1.55	4272	744	847	867	332
BR-56	Composita	-5.16	1.85	2997	493	732	819	351

ISOTOPE STRATIGRAPHY

Figures 4-3 and 4-4 show the individual data points and lines of means for unaltered brachiopods and corresponding matrices. Cement data, which were obtained within the shells of brachiopods, are included for comparison purposes. At Jemez Springs, the cements have the lightest $\delta^{18}O$ values relative to matrix and brachiopod shells at coeval horizons (Fig. 4-3). On the average, however, matrix is lighter by about 1‰ than their brachiopod counterparts. This suggests that in consideration of horizon-by-horizon brachiopods have retained the heaviest $\delta^{18}O$ values, and should better represent depositional aspects of the ambient sea water (cf. Lowenstam, 1961; Brand, 1994).

Cements from the Battleship Rock section exhibit the similar $\delta^{18}O$ trends to those at Jemez Springs (Fig. 4-4). In all instances, matrix is more negative than that of corresponding brachiopods. Since the brachiopods have been treated as unaltered, then the cement and matrix data must represent diagenetic signatures. Consequently, it is reasonable to infer that no uniform or constant relationship exists between unaltered brachiopods and the altered matrices. The $\delta^{18}O$ values between brachiopods (N=65) and matrices (N=14) vary from a low of o.1‰ to a high of 3.0‰. Because of this, it is questionable by using a correction factor to adjust matrix data, and to compare it with that of brachiopods.

Similar observations have been made for the $\delta^{13}C$ data of cements, matrices and brachiopods (Fig. 4-5). The mean $\delta^{13}C$ values vary from a low of 0.2‰ to a high of 6.7‰. The difference between brachiopod and matrix $\delta^{13}C$ trends suggests that matrix may, at best, represent only a first-order relationship

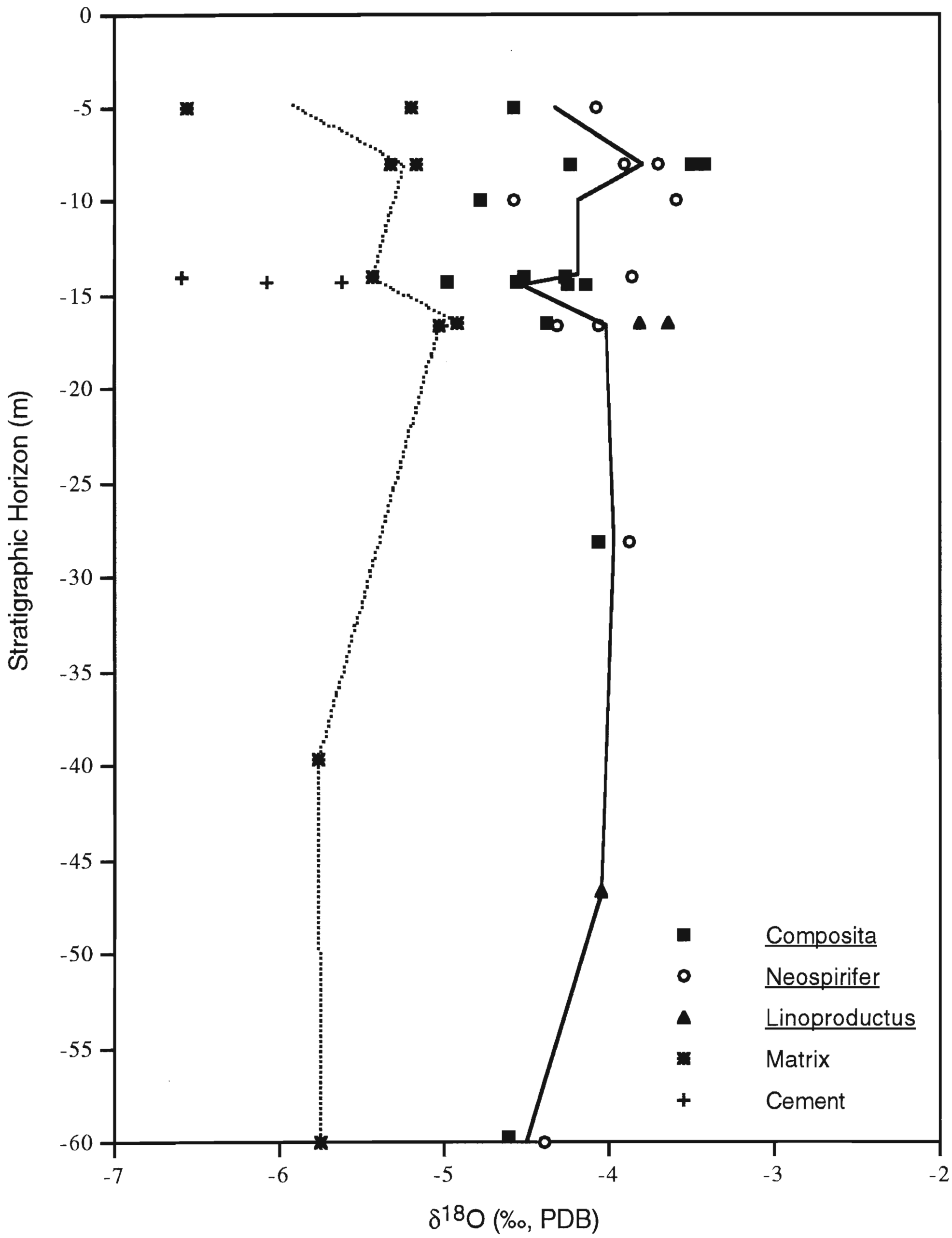


Fig. 4-3 Stratigraphic variation of $\delta^{18}O$ for samples from Jemez Springs. Solid and dashed lines represent mean values of brachiopod and matrix for each horizon.

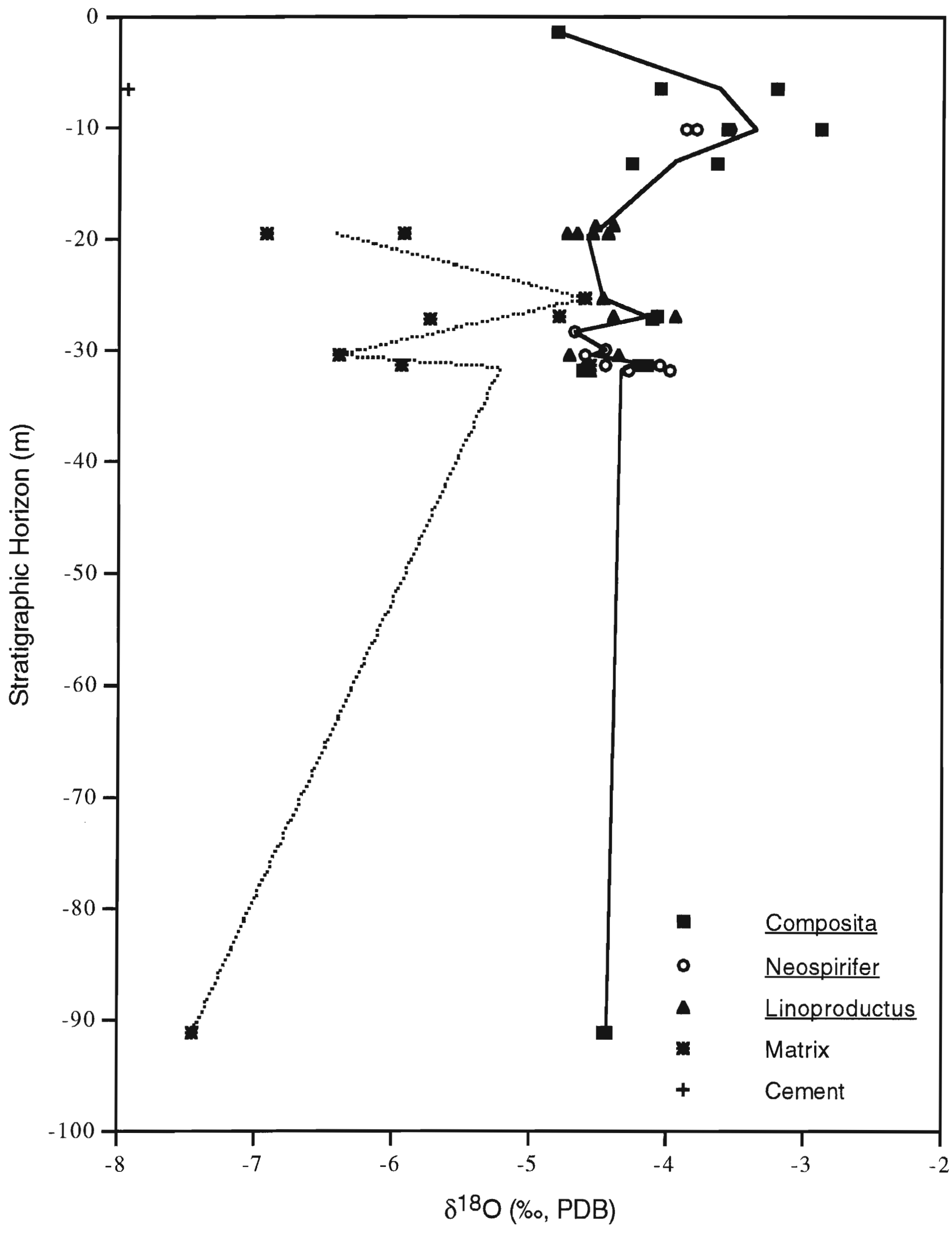


Fig. 4-4 Stratigraphic variation of $\delta^{18}O$ for samples from Battleship Rock. Solid and dashed lines represent mean values of brachiopod and matrix for each horizon.

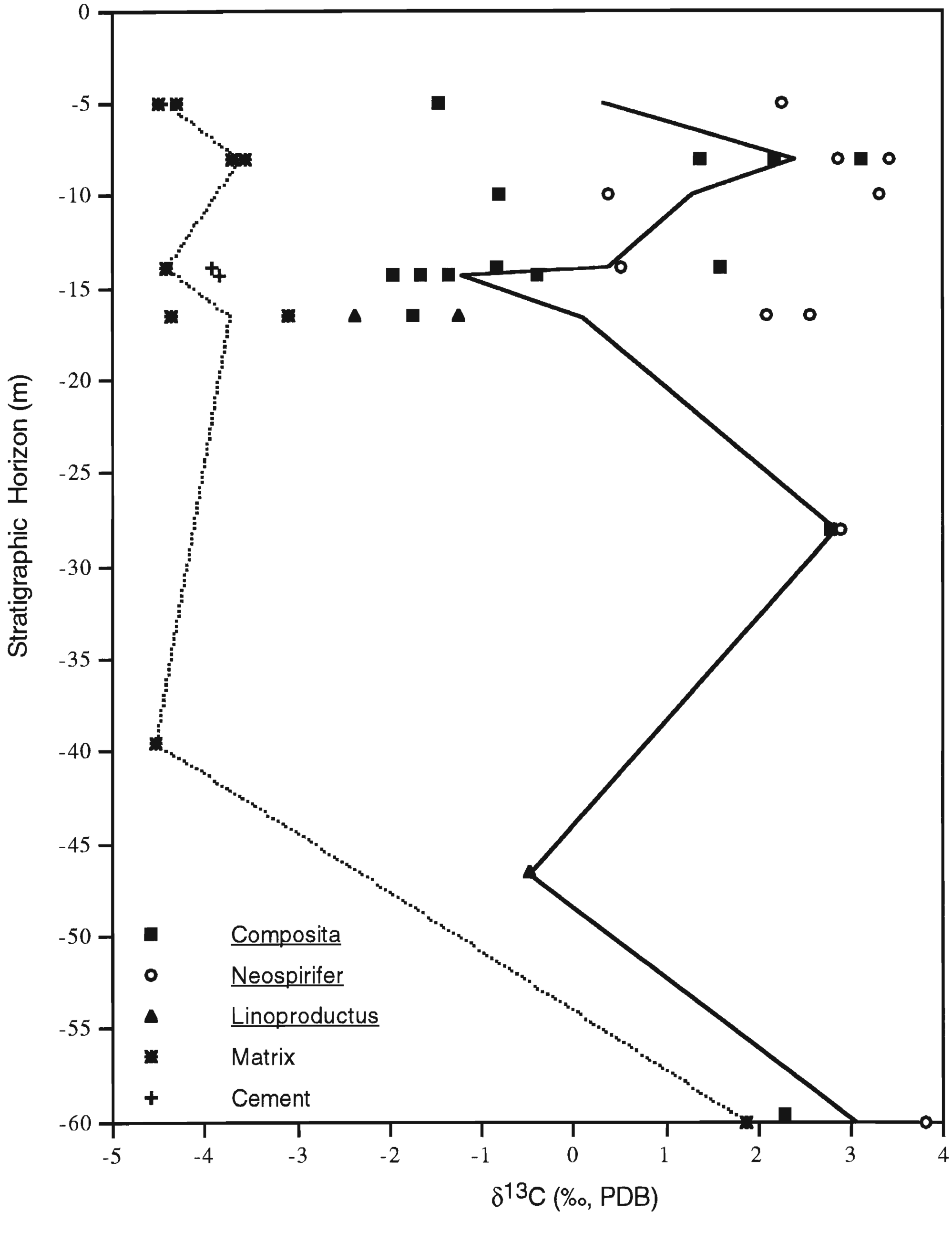


Fig. 4-5 Stratigraphic variation of $\delta^{13}C$ for samples from Jemez Springs. Solid and dashed lines represent mean values of brachiopod and matrix, respectively.

of depositional aspects. Brachiopod data are clearly superior to matrix in defining depositional parameters and conditions.

Grossman et al. (1993) studied brachiopods from shale layers of the Jemez Springs Member of the Madera Formation. Because their stratigraphic control is difficult to ascertain, scatter plots have to be used. A comparison between the brachiopod data of this study and that of Grossman et al. (1993) from Jemez Springs shows a clear separation into distinct fields (Fig. 4-6). The distinction relates mainly to the $\delta^{13}C$ values but not in $\delta^{18}O$ values. One possible explanation may be differences in sampling and lithological examination. In this study, fossils and matrix were collected from both shale and limestone of the whole Madera Formation, while Grossman et al. (1993) limited their collecting of brachiopods to just shale horizons of the Jemez Springs Member. This different collecting procedure probably accounts for the observed isotopic differences between the two populations.

Isotopic evaluation of brachiopods from other stratigraphic sections shows a similar distribution pattern (Fig. 4-7). The data from Jemez Springs and Battleship Rock of this study overlap significantly in both $\delta^{13}C$ and $\delta^{18}O$. In contrast, samples from Hot Springs (cf. Fig. 4-7) show the same pattern, but higher $\delta^{13}C$ values. The reason for such dichotomy among different populations may be the same as noted above.

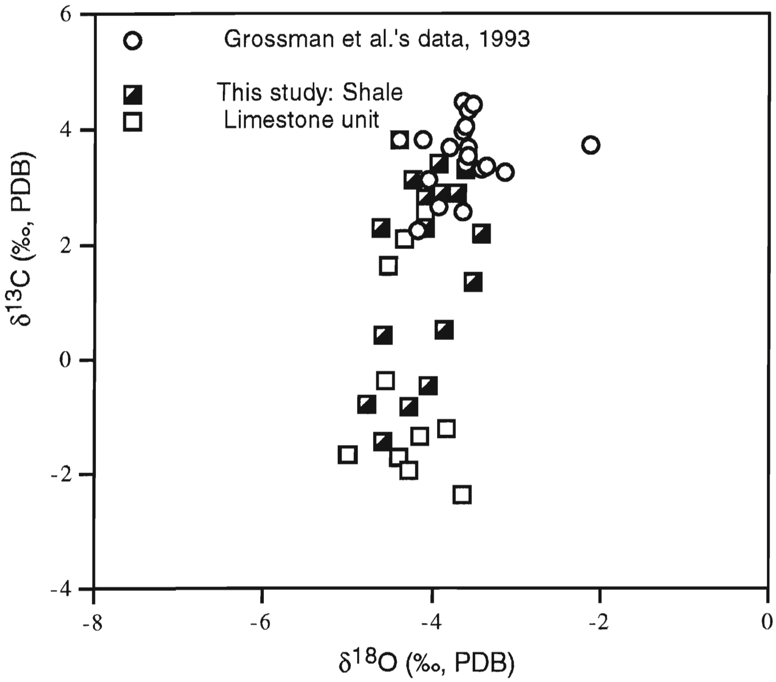


Fig. 4-6 Isotopic comparison of brachiopods from Jemez Springs, Madera Formation.

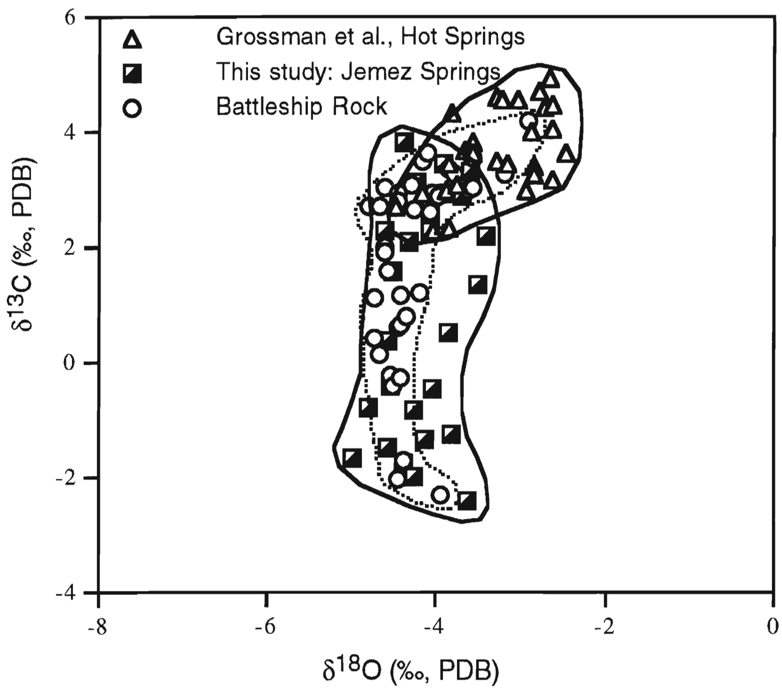


Fig. 4-7 Isotopic comparison of brachiopods among different sections from the Madera Formation.

Biogenic fractionation or vital effects in brachiopods may seriously limit the use of brachiopod-derived isotope values in defining stratigraphic trends. As expected, there is a considerable overlap in $\delta^{18}O$ values of Composita (Fig. 4-8) and Neospirifer (Fig. 4-9) from Jemez Springs, Battleship Rock and Hot Springs. The $\delta^{13}C$ values, however, show a slight spread among these sections (Figs. 4-8 & 4-9). It is not clear whether this variation reflects a vital effect or is related to depositional environments (Bates & Brand, 1991). Since a single genus is used in the plots, then a generic vital effect can be discounted as a factor responsible for the observed $\delta^{13}C$ variation, indicating that these brachiopods incorporated oxygen and carbon isotopes in equilibrium into their shell calcites (cf. Lowenstam, 1961; Adlis et al., 1988; Brand, 1989). The subject will be further evaluated statistically in the next chapter.

SUMMARY

The Madera brachiopods from Jemez Springs, Battleship Rock sections have preserved pristine stable isotope compositions in their shell calcites. Stratigraphic comparison between brachiopods and matrix (and cements) shows that brachiopods are superior to their coeval matrix material in defining paleoenvironmental parameters. In addition, the temporal and spatial analyses support the hypothesis of isotopic equilibrium incorporation for Composita and Neospirifer, from the Upper Pennsylvanian Madera Formation.

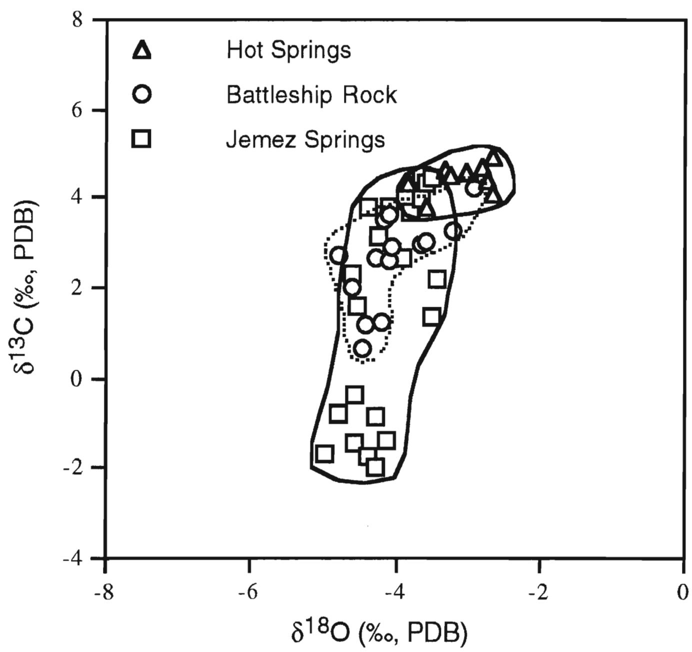


Fig. 4-8 Isotopic comparison of <u>Composita</u> from the Madera Formation

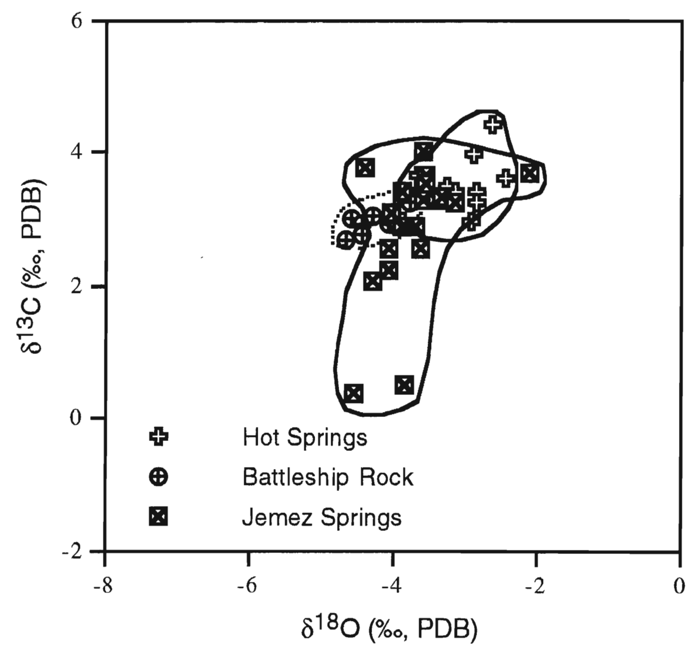


Fig. 4-9 Isotopic comparison of <u>Neospirifer</u> from the Madera Formation

Chapter 5

STATISTICAL ANALYSIS OF BRACHIOPODS FROM THE MADERA FORMATION

INTRODUCTION

Statistics is a powerful tool in compiling geochemical data, because all measurements contain experimental errors and are normally distributed. It may not be able to answer these questions such as "Is this number anomalous or normal?" and "Are there differences between the Jemez Springs and Battleship Rock sections?", but we can draw some conclusions with certain assurance by using statistical methods.

On carbonate diagenesis, Brand and Veizer (1980) were the first to apply factor analysis to their samples. From the Read Bay Formation and Burlington Limestone they demonstrated that the degree of diagenesis could be determined from the covariance of Sr^{2+} and Mn^{2+}. For low-Mg calcite, because of its stability in both marine and meteoric water environments, factor analysis showed that the diagenetic equilibration is the dominant factor (cf. Brand & Veizer, 1980).

In this study, three brachiopod genera (Composita, Neospirifer and Linoproductus) and a large number of matrices from the Jemez Springs and Battleship Rock sections were analyzed. Although trace elemental and isotopic analyses have already furnished important information, the author is interested in evaluating further the geochemical data statistically in order to get a more comprehensive picture of environmental and diagenetic events.

VARIABLE SELECTION

Tables 5-1 and 5-2 summarize the trace element (Ca, Mg. Sr, Na, Fe, Mn, Zn, and Cd) and stable isotope ($\delta^{18}O$ and $\delta^{13}C$) compositions for the various allochems and constituents of the Madera Formation. The brachiopods from the two sections exhibit similar mean values for Mg, Sr and Na (Composita and Neospirifer) and slight differences for the other elements. The elemental contents of Linoproductus are difficult to assess because of the paucity of data from Jemez Springs (Table 5-1). Of equal interest is the higher Mg content in crinoids, cements and matrix from Battleship Rock, which is a diagenetic phenomenon related to dolomitization within this interval and section (cf. Chapter 3).

The stable isotope composition of the brachiopods share common trends for $\delta^{18}O$, with more variable $\delta^{13}C$ values (Table 5-2). Altered components such as crinoids, cements and matrices are greatly different from the preserved brachiopods, with a difference of about 1~2‰ in $\delta^{18}O$ and about 1~8‰ in $\delta^{13}C$ (Table 5-2). As already demonstrated previously, this underlines again the weakness of using cement and matrix-derived $\delta^{13}C$ or $\delta^{18}O$ values as indicators for depositional aspects (Brand, 1994).

Table 5-1 Summary statistics (mean and standard deviation) of trace elemental data from the Madera Formation

CATEGORY	Number	Mg (ppm)	Sr (ppm)	Na (ppm)	Fe (ppm)	Mn (ppm)	Zn (ppm)	Cd (ppb)
Mean Values								
Composita								
JS section	20	1315	425	1466	76	264	8	352
BR section	26	1872	539	832	218	114	10	967
Neospirifer								
JS section	21	1327	600	1576	166	149	21	236
BR section	19	1498	662	885	179	60	6	88
Linoproductus								
JS section	4	2462	802	795	124	168	21	177
BR section	27	3544	836	728	414	259	18	1918
Crinoid								
JS section	2	1952	526	1535	101	122	10	667
BR section	7	6704	665	246	675	271	6	147
Cement								
JS section	3	925	272	1217	97	1014	1	281
BR section	6	5347	545	118	491	593	18	596
Matrix								
JS section	29	1825	415	875	301	657	16	607
BR section	51	9282	733	437	1376	443	17	803
Standard Deviation								
Composita								
JS section	20	353	70	326	34	178	9	249
BR section	26	696	96	238	186	83	7	4045
Neospirifer								
JS section	21	581	76	549	157	163	28	270
BR section	19	458	64	201	112	32	4	87
Linoproductus								
JS section	4	497	240	726	67	58	21	169
BR section	27	691	135	240	192	240	12	4816
Crinoid								
JS section	2	81	80	115	1	10	3	11
BR section	7	728	70	29	747	237	5	84
Cement								
JS section	3	65	64	62	37	66	1	47
BR section	6	2750	76	45	128	266	14	284
Matrix								
JS section	29	664	199	631	157	422	15	386
BR section	51	4926	229	361	650	135	9	514

Table 5-2 Summary statistics of isotopic data from the Madera Formation

CATEGORY	Number	$\delta^{18}O$ (‰, PDB) Mean	SD	$\delta^{13}C$ (‰, PDB) Mean	SD
Composita					
JS section	14	-4.310	0.438	0.216	1.886
BR section	14	-4.039	0.535	2.592	1.013
Neospirifer					
JS section	11	-4.084	0.329	1.965	1.823
BR section	10	-4.178	0.378	3.036	0.261
Linoproductus					
JS section	3	-3.840	0.201	-1.367	0.956
BR section	13	-4.494	0.207	-0.025	1.326
Crinoid					
JS section	1	-5.240		-5.140	
BR section	4	-5.240	0.802	1.560	0.420
Cement					
JS section	3	-6.100	0.480	-3.873	0.058
BR section	4	-6.628	2.273	-1.335	2.179
Matrix					
JS section	7	-5.501	0.523	-4.213	0.398
BR section	7	-6.727	1.055	-0.681	1.800

Since trace elements are lognormally distributed in biogenic carbonates (Veizer & Demovic, 1974), their lognormal values were chosen as statistical variables in factor analysis. 215 trace element samples (including fossils, matrix and cement) and 91 isotope samples were selected for statistical analysis. Due to the fact that the specimens are represented by three brachiopod genera from two localities, it is also necessary to choose fossil genera and sections as basic variables. From a statistical point of view, these variables should be stable and independent. We did not test the data before our statistical work, however, such a big sample population should meet the basic requirements for statistics.

FACTOR ANALYSIS

The basic principle of factor analysis is able to reduce or rearrange the correlation coefficient array to a smaller set of factors which are interpreted as the source variables (R-type) or source individuals (Q-type) for the statistical data (cf. Kim, 1975). Therefore, the first factor may be taken as the best linear combination of independent variables existing in the data. The second factor is viewed as the second best combination of independent variables, and so forth. Because there are three dichotomies in the method itself (cf. Kim, 1975; Table 24.1), R-type correlation matrix, common-factor model and varimax rotation were chosen for factor analysis.

The basic model for common-factor analysis can be expressed as:

$$Z_i = a_{i1}F_1 + a_{i2}F_2 + \ldots + a_{ij}F_j + d_iU_i \qquad (5\text{-}1)$$

$$i = 1,2,\ldots,n; \quad j = 1,2,\ldots,m; \quad and\ i \neq j$$

where Z_i stands for variables, F_j for factors, and a_{ij} for the standardized multiple-regression coefficient of variable i on factor j, i.e., the factor loadings. Because we choose varimax rotation which maximizes the variance of the squared loadings in each column, the last term in equation 5.1, the unique portion of variable i would become zero. Thus, any correlation between two variables is postulated due to the common factor (cf. Kim, 1975). For convenience, results of factor analysis are discussed by individual sections.

Factor data presented in Tables 5-3 to 5-6 are limited to those with eigenvalues greater than 1.00000, and individual parameters with values greater than 0.40000. Generally, communality values explain the total variation discernible by factor analysis.

Jemez Springs

Factor analysis of matrix samples from the Jemez Springs section shows that two factors explain the observed geochemical variation and trends (Table 5-3). The first factor is loaded on Fe and Mn, with minor importance placed on Sr. This is interpreted to represent diagenetic stabilization of the originally metastable carbonate sediments (Brand & Veizer, 1980). The second factor with major loading on Mg and Fe represents a secondary phase of diagenetic alteration such as dolomitization. This secondary phase probably involves the redistribution of Mg into previously Mg-poor sediments.

For the preserved brachiopods from Jemez Springs three factors account for the observed geochemical variation (Table 5-4). The first factor is ascribed to habitat variation in ambient water conditions which indirectly influenced growth parameters (Brand & Logan, 1991). The second factor with loading of Fe and Zn is probably related to redox variation of the ambient seawater and possibly supply of these specific elements. The third factor, with major loading on $\delta^{13}C$, Sr, Mn and Cd, and minor loading on $\delta^{18}O$, is probably related to continentality of the site during Jemez Springs time and/or seawater productivity. This co-variance between Mn and continental influences is similar to that observed in modern brachiopod populations (cf. Brand & Logan, 1991).

Table 5-3 Factor analysis (correlation matrix, common-factor model, varimax rotated) of matrix samples (N=35) from Jemez Springs

	Factor 1	Factor 2	Communality
log Ca	-0.01488	-0.10331	0.42346
log Mg	-0.05868	0.91183	0.90363
log Sr	-0.31507	0.14722	0.71964
log Na	0.04743	-0.19499	0.90671
log Fe	0.53058	0.64060	0.86784
log Mn	0.86277	-0.00909	0.93248
log Zn	-0.07530	0.35070	0.93502
log Cd	0.29948	0.30251	0.75409
Eigenvalue	2.75699	2.01223	
% Variance	15.33036	19.08420	

Interpretation:

Factor 1	Diagenetic alteration
2	Alteration /Dolomitization

Table 5-4 Factor analysis (correlation matrix, common-factor model, varimax rotated) of preserved brachiopods (N=24) from Jemez Springs

	Factor 1	Factor 2	Factor 3	Communality
$\delta^{18}O$	-0.17181	-0.19941	0.33650	0.80237
$\delta^{13}C$	-0.66202	0.01293	0.47570	0.77535
log Ca	0.51269	-0.25404	-0.15119	0.73606
log Mg	0.79448	0.37812	0.12329	0.83174
log Sr	-0.03597	0.07519	0.90976	0.88907
log Na	-0.09170	-0.23645	0.25904	0.95182
log Fe	0.18244	0.91586	-0.02425	0.91933
log Mn	0.14952	0.08947	-0.51443	1.00000
log Zn	-0.00582	0.58113	0.19800	0.84627
log Cd	0.48279	0.15213	-0.46288	0.82289
Eigenvalue	3.50669	2.58485	1.27661	
% Variance	16.60300	15.16649	17.91033	

Interpretation:

Factor 1	Habitat
2	Oxidation-reduction potential
3	Continentality or seawater productivity

Battleship Rock

Matrix samples from the Battleship Rock section are also characterized by two factors (Table 5-5). Factor 1 is heavily loaded on Mg, Sr, Na and Fe which is interpreted to represent the diagenetic process of secondary (mixed water) dolomitization. Factor 2, with exclusive loading on Sr and Mn distribution, is interpreted as representing post-depositional diagenesis in the presence of continental waters.

Three factors describe the geochemical variation observed in the brachiopods from this locality (Table 5-6). In this instance, Factor 1 is loaded on Fe and $\delta^{18}O$, and is interpreted to reflect aerobic variations of the ambient seawater. The second factor, with its major loading on Na and $\delta^{13}C$, probably represents some environmental habitat control by seawater composition. The third factor is loaded singularly on Ca and as such probably reflects the partial silicification of the brachiopod shells.

t-TEST

Student's *t*-test is usually used to express confidence intervals and for comparing mean values from a normally distributed population (cf. Sokal & Rohlf, 1981; Harris, 1991). For the two sets of data we compute the *t*-variate by:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s} \sqrt{\frac{n_1 \times n_2}{n_1 + n_2}} \qquad (5\text{-}2)$$

where $\bar{x}$ is the mean of measurements for two sets, and n is the number of

Table 5-5 Factor analysis (correlation matrix, common-factor model, varimax rotated) of matrix samples (N=53) from Battleship Rock

	Factor 1	Factor 2	Communality
log Ca	-0.01407	0.06253	0.19283
log Mg	<u>0.87485</u>	0.26117	0.87092
log Sr	<u>0.55358</u>	<u>0.75117</u>	1.00000
log Na	<u>0.57693</u>	-0.11105	0.66332
log Fe	<u>0.95959</u>	-0.11126	1.00000
log Mn	0.10290	<u>-0.93417</u>	0.94813
log Zn	0.13366	0.10595	0.41622
log Cd	0.06024	0.00640	0.25840
Eigenvalue	2.73708	1.50972	
% Variance	29.47197	19.31271	

Interpretation:
Factor 1 Dolomitization
2 Diagenetic alteration

Table 5-6 Factor analysis (correlation matrix, common-factor model, varimax rotated) of preserved brachiopods (N=35) from Battleship Rock

	Factor 1	Factor 2	Factor 3	Communality
$\delta^{18}O$	<u>-0.77830</u>	0.01383	0.06880	0.73616
$\delta^{13}C$	-0.29027	<u>0.55923</u>	0.30101	1.00000
log Ca	-0.01501	0.05919	<u>0.64517</u>	0.43317
log Mg	0.35194	-0.26240	-0.01615	0.97409
log Sr	0.34711	-0.06502	-0.25727	0.93134
log Na	-0.05153	<u>0.84499</u>	0.04384	0.73940
log Fe	<u>0.77088</u>	-0.21802	0.06834	0.92086
log Mn	0.22596	-0.14436	0.08649	0.81636
log Zn	0.28184	0.09910	0.05726	0.69137
log Cd	0.30974	-0.23682	0.34963	0.81397
Eigenvalue	5.13342	1.04105	0.86219	
% Variance	17.57928	12.37806	7.17621	

Interpretation:
Factor 1 Oxidation-reduction potential
2 Habitat
3 Silicification

observations. The value of s is a pooled standard deviation, and

$$s = \sqrt{\frac{\sum_{set1}(x_i - \bar{x}_1) + \sum_{set2}(x_j - \bar{x}_2)}{n_1 + n_2 - 2}} \qquad (5\text{-}3)$$

where $n_1 + n_2 - 2$ is the degree of freedom. Thus, if the calculated t is greater than the tabulated t (e.g., Rohlf & Sokal, 1981), the two sets of data are considered to be significantly different at the determined confidence level. Otherwise, the conclusion will be rejected (cf. Harris, 1991).

In this study, It was deemed important to test the differences between the brachiopod genera, and two stratigraphic sections. The null hypotheses could be expressed as: Are there significant differences between different brachiopod genera? Or, are there significant differences within the same brachiopod genus from the Jemez Springs and Battleship Rock sections? Since Linoproductus is not well represented in the samples (cf. Chapters 3 and 4) only Composita and Neospirifer will be used for t-test analysis.

For a true test of biological fractionation and vital effect, it is important to equalize the data from a spatial and temporal perspective. That is to say, habit variations such as water chemistry, temperature and salinity must be minimized. The spatial parameter is usually satisfied by collecting samples from one outcrop for comparison, but the temporal parameter is normally neglected. However, these two concepts have to be considered equally because the temporal parameter is as important as the spatial one in defining "real" and "realistic" fractionation effects in marine organisms such as brachiopods (Brand & Logan, 1991).

t-test results between Composita and Neospirifer from the two localities are presented in Tables 5-7 to 5-10. At the 95% confidence level, $\delta^{13}C$, Sr, Mn and Cd are significantly different in Composita vs. Neospirifer from Jemez Springs (Table 5-7), but no significant differences for these elements, except for Sr, were recognized in Battleship Rock (Table 5-8). The observed significance may not be related to biological fractionation or vital effects, because specimens of the two genera may not all come from coeval sampling horizons. Furthermore, the significant differences between different genera at the same locality (Tables 5-7 & 5-8) are similar to those observed within the single genus at different localities (Tables 5-9 & 5-10). This provides strong evidence that there is no observable vital effect operative for $\delta^{18}O$ and $\delta^{13}C$ in these two brachiopod genera (cf. Brand, 1989; Bates & Brand, 1991). Instead, variances observed in $\delta^{13}C$ and Sr, Mn, Cd from Jemez Springs are probably a result of comparing samples from different stratigraphic horizons, or might be related to different degrees of preservation according to Brand and Veizer's (1980) diagenetic model (cf. Chapter 3).

The argument for temporal-environmental shift influences on trace element contents and stable isotope compositions is also supported by the *t*-test evaluation of single brachiopod genus for the two localities (Tables 5-9, 5-10). For Composita, significant differences were noted for $\delta^{13}C$, Sr, Na and Mn between the two localities, whereas for Neospirifer, the elements are Ca and Na. This invariance in correlation must reflect local variations in environmental conditions. Thus, spatial and temporal co-variance while considering environmental aspects is of utmost importance in deciphering the vital effects in fossil marine invertebrates.

Table 5-7 *t*-test of preserved Composita vs. Neospirifer from Jemez Springs

Element & Isotope	Number of Observation	*t*-stat	Degree of Freedom	Significance	Critical Values $t_{.05}$ [21]
$\delta^{18}O$	14				
	9	1.775	21	0.090	**2.080**
$\delta^{13}C$	14				
	9	3.131	21	0.005	
logCa	14				
	9	0.638	21	0.530	
logMg	14				
	9	1.197	21	0.245	
logSr	14				
	9	5.834	21	0.000	
logNa	14				
	9	1.850	21	0.078	
logFe	14				
	9	0.557	21	0.583	
logMn	14				
	9	2.329	21	0.030	
logZn	14				
	9	0.632	21	0.534	
logCd	14				
	9	2.090	21	0.049	

Table 5-8 *t*-test of preserved Composita vs. Neospirifer from Battleship Rock

Element & Isotope	Number of Observation	*t*-stat	Degree of Freedom	Significance	Critical Values $t_{.05}$ [20]
$\delta^{18}O$	13				
	9	1.085	20	0.291	**2.086**
$\delta^{13}C$	13				
	9	1.298	20	0.209	
logCa	13				
	9	1.558	20	0.135	
logMg	13				
	9	0.805	20	0.430	
logSr	13				
	9	2.774	20	0.012	
logNa	13				
	9	1.264	20	0.221	
logFe	13				
	9	0.232	20	0.819	
logMn	13				
	9	1.319	20	0.202	
logZn	13				
	9	1.576	20	0.131	
logCd	13				
	9	0.913	20	0.372	

Table 5-9 *t*-test of preserved Composita between Jemez Springs and Battleship Rock

Element & Isotope	Number of Observation	*t*-stat	Degree of Freedom	Significance	Critical Values $t_{.05}$ [25]
$\delta^{18}O$	14				
	13	1.814	25	0.082	**2.060**
$\delta^{13}C$	14				
	13	<u>3.982</u>	25	0.001	
logCa	14				
	13	2.289	25	0.031	
logMg	14				
	13	2.252	25	0.033	
logSr	14				
	13	<u>4.284</u>	25	0.000	
logNa	14				
	13	<u>4.415</u>	25	0.000	
logFe	14				
	13	2.395	25	0.024	
logMn	14				
	13	<u>3.654</u>	25	0.001	
logZn	14				
	13	0.669	25	0.510	
logCd	14				
	13	2.414	25	0.023	

Table 5-10 *t*-test of preserved Neospirifer between Jemez Springs and Battleship Rock

Element & Isotope	Number of Observation	*t*-stat	Degree of Freedom	Significance	Critical Values $t_{.05}$ [16]
$\delta^{18}O$	9				
	9	1.122	16	0.278	**2.120**
$\delta^{13}C$	9				
	9	1.473	16	0.160	
logCa	9				
	9	<u>2.181</u>	16	0.044	
logMg	9				
	9	2.113	16	0.051	
logSr	9				
	9	1.616	16	0.126	
logNa	9				
	9	<u>4.231</u>	16	0.001	
logFe	9				
	9	1.782	16	0.094	
logMn	9				
	9	1.299	16	0.212	
logZn	9				
	9	1.000	16	0.332	
logCd	9				
	9	0.837	16	0.415	

SUMMARY

Using statistical analyses to the geochemical data from the Madera Formation, the previous microstructural, trace elemental and stable isotopic conclusions with regard to the diagenetic event, preservation state and depositional environment are confirmed. *t*-test results that the significance between different genera at the same locality is similar to that of the same genus at different localities, furthermore, unequivocally support the earlier assertion that the Madera brachiopods do not exert a vital control over their $\delta^{18}O$ and $\delta^{13}C$ compositions.

DISCUSSION AND CONCLUSION

When using LMC fossil shells (e.g., brachiopods, mollusks) as proxy indicators for obtaining information about ancient ocean water chemistry, two critical questions are frequently raised. First, what is the preservation state of fossil shells or skeletons after diagenetic alteration? Secondly, is there a possibility of biogenic fractionation or "vital effects" in the organisms, because brachiopod shells are not direct precipitates from seawater.

To answer the first question, a group of authors suggested that a multiple geochemical approach (i.e., mineralogy, microstructure, trace elements and stable isotopes) would be the best way to evaluate the degree of diagenetic alteration (e.g., Brand and Veizer, 1980; Veizer, 1983; Veizer et al., 1986; Brand, 1989; Bates & Brand, 1991; Brand, 1994). Other investigators proposed that cathodoluminescent (CL) methods might provide quicker and more accurate information on the diagenetic preservation (e.g., Popp et al., 1986; Adlis et al., 1988; Carpenter et al., 1991; Woo et al., 1993; Grossman et al., 1993).

To resolve the second problem, Lowenstam (1961) and Lepzelter et al. (1983) reported that articulate brachiopods, as old as Mississippian, precipitated their shell calcite in oxygen isotopic equilibrium or very closely in equilibrium with ambient seawater, but questions still remain (cf. Veizer et al., 1986; Rush & Chafetz, 1990) because of the poor understanding of biochemical processes in brachiopod shell secretion. To avoid such difficulties, some authors focused on abiotic marine cements (e.g., Given & Lohmann, 1985;

Carpenter et al., 1991). Nevertheless, synsedimentary cements, commonly aragonite or HMC, are not resistant to diagenetic alteration (cf. Rush & Chafetz, 1990). Articulate brachiopods, therefore, are considered as the best material to be used in Paleozoic paleoceanographic studies (cf. Veizer et al., 1986; Popp et al., 1986).

DIAGENETIC PRESERVATION

"Preservation, in the strictest sense, infers in all instances not only preservation of macro- and microstructures of carbonate allochems, but also of the original mineralogy and geochemistry of the endo/exoskeleton shell" (cf. Brand, 1994; p.217). According to this definition diagenetic assessment should be a process when one deals with fossil samples. Diagenetic preservation hence cannot be determined only by physical methods. For example, one cannot fully recognize diagenetic alteration by thin section or petrographic observation. Adlis et al. (1988) demonstrated that some petrographically well preserved brachiopods still exhibited significant changes in shell geochemistry. Rush and Chafetz (1990) reported that some petrographically fabric-retentive brachiopods had undergone chemical alteration, but did not display a recrystallized fabric. Use of SEM has greatly widened our outlook but, unfortunately, microstructural information cannot always ascertain the whole spectrum of diagenetic alteration because the primary layer of shells are generally lacking (cf. Bates, 1989). Therefore, microstructural observations are deemed most reliable only if supplemented by chemical evaluation.

Cathodoluminescence has been used in examining the preservation of Paleozoic brachiopods, and was reported as a tool for the fast recognition of diagenetic alteration (cf. Popp et al., 1986). The principle of this method is based on the incorporation of Mn^{2+} and Fe^{2+} into fossil shell calcites. Because unaltered modern brachiopods are typically non-luminescent, although this is not always the case (cf. Brand & Logan, 1991), it is assumed by analogy that the luminescent Devonian brachiopods have been undergone diagenetic recrystallization (cf. Popp et al., 1986; Rush & Chafetz, 1990). However, many recent studies have demonstrated that the function of cathodoluminescence may be exaggerated in assessing the degree of diagenetic preservation. For instance, Rush and Chafetz (1990) furnished evidence from the Devonian Helderberg strata of New York State that fabric-retentive, non-luminescent brachiopods were diagenetically altered. Brand (1994) showed that modern unaltered biogenic aragonite has differential luminescence, implying chemical variations due to environmental controls. As such, the cathodoluminescence method may be a useful tool in distinguishing calcite from dolomite, but it may not be so diagnostic in evaluating preservation (cf. Brand, 1994).

To test the preservation state and degree of the Madera Formation, a step-by-step method which follows the multiple geochemical approach was carried out. Because of the limitation of SEM observations (cf. Chapter 2), the geochemical data were particularly focused on. 249 trace elemental and 103 isotopic samples, including brachiopod shells, crinoids, cements and matrices, provide a comparative reference for such an evaluation. According to microstructural and trace elemental criteria, 21 diagenetically altered samples of 132 brachiopods were recognized and eliminated from the data base (Table 3-2). Based on isotopic criteria, 7 additional altered samples of 72 brachiopods were identified and discarded from further consideration (Table 4-2). If we vested these two criteria with equal weight, then the degree of diagenetic alteration for the Madera brachiopods will correspond to about 14%. In other words we can reasonably expect that in the Madera Formation, 86% of brachiopod samples would be well-preserved.

Grossman et al. (1993) calculated that 79% of Composita, 86% of Neospirifer and 17% of Cruruthyris from the Madera Formation were suitable for isotopic study, with an average of 61% (cf. Grossman et al., 1993; Table 1). It is difficult to ascertain what is the major cause for such a difference. In addition to different procedure in collecting specimens (cf. Chapter 4), perhaps, the different methods in evaluating the degree of diagenetic alteration may account for this difference.

VITAL EFFECTS

The biogenic isotope fractionation or "vital effects" of brachiopods has been widely discussed, but has yet not been resolved (cf. Veizer et al., 1986; Popp et al., 1986; Adlis et al., 1988; Brand, 1989; Bates & Brand, 1991; Carpenter et al., 1991; Grossman et al., 1993). To minimize or avoid vital effects, Adlis et al. (1988) attempted to use a single species of articulate brachiopod. However, It may be worth to recall Erez's field experiment for foraminifera and corals which was conducted in the Gulf of Eilat, Israel in 1975. The fundamental design of that experiment was testing different species at the same water depth and the same species at different water depth with ^{45}Ca and ^{14}C tracers (Erez, 1978). The observations suggested that isotopically lighter variations, for both oxygen and carbon, were caused by a "vital effect" involving metabolic activity in skeleton secretion (Erez, 1978).

Mimicking Erez's experiment, it might be interesting to discuss vital effects of brachiopods from the Madera Formation, because we analyzed three brachiopod genera at two different sections. In other words, in order to check vital effects one could compare the isotopic composition of brachiopods by using different genera at same locality and same genus at different localities. Such a comparison depends mainly on two assumptions: 1) Modern and ancient brachiopods secrete their calcite shells in isotopic equilibrium with ambient seawater; biogenic fractionation, if any, may be constant and can be accounted for (cf. Lowenstam, 1961); 2) Lighter isotopic composition of the brachiopod shells cannot be simply interpreted as seasonal variations and different water depth habitats, but could be caused by vital effects (cf. Erez, 1978; Rush & Chafetz, 1990).

The mean $\delta^{18}O$ difference between Composita and Neospirifer at the Jemez Springs section is about 0.2‰, with a corresponding average of about 0.1‰ from Battleship Rock (cf. Table 5-2). Between the two localities, the mean $\delta^{18}O$ differences are about 0.3‰ for Composita, and about 0.1‰ for Neospirifer (cf. Table 5-2). This seems to suggest that no vital effect was yielded, because there are no distinct differences in isotope values between brachiopod genera, nor from the two stratigraphic sections. Nevertheless, the mean $\delta^{13}C$ differences range from 0.4‰ to 1.7‰ for inter-generic comparisons at the same section, and from 1.1‰ to 2.4‰ for a single genus at different localities (cf. Table 5-2), indicating that habitat and spatial variations must be considered in the variation. Since biogenic carbon isotopic fractionation is more complex than oxygen (cf.

Schidlowski, 1986), the $\delta^{13}C$ difference between Composita and Neospirifer may not simply be a reflection of a vital effect. This controversy rages about the $\delta^{13}C$ composition of brachiopod shell calcites (cf. Veizer et al., 1986; Popp et al., 1986; Brand, 1989; Bates & Brand, 1991). The key point is, that in many cases, data are compared even though they come from different horizons.

Grossman et al. (1993) discussed their isotopic values of brachiopods from Texas, Kansas and New Mexico. They recognized an average isotopic shift of 0.3‰ for the same species for both $\delta^{18}O$ and $\delta^{13}C$, and $\delta^{13}C$ values of Composita ranged from 0.6‰ to 1.5‰. Comparing the shell morphology, they argued that a vital effect on $\delta^{18}O$ of brachiopods was minimal, whereas the $\delta^{13}C$ shift might be caused by the biomineralization process (cf. Grossman et al., 1993).

Supporting evidence for an equilibrium process for both $\delta^{13}C$ and $\delta^{18}O$ is provided by using horizon-by-horizon comparisons and statistical tests. The great overlap in $\delta^{18}O$ datum points for both Composita and Neospirifer from three different localities suggested that vital effects might not be responsible for the isotopic variation (cf. Figs. 4-8 & 4-9). A more plausible explanation for the observed trend and distribution is one or several local environmental aspects between the localities and/or temporal horizons, and this was really confirmed by t-test (cf. Chapter 5). Overall, in the studied Upper Pennsylvanian Madera brachiopods, there are no significant vital effects over their $\delta^{13}C$ and $\delta^{18}O$ compositions. The observed $\delta^{13}C$ variation, is probably related to both temporal and environmental variations.

CONCLUSIONS

This research has come to the following conclusions:

a) Despite diagenetic/geological processes overprinting of the carbonate constituents, the state and degree of preservation for the Upper Pennsylvanian Madera Formation have been determined. In general, variation in degree and range of diagenetic alteration are not only observed within the two stratigraphic sections (Jemez Springs & Battleship Rock), but also within a single fossil shell.

b) About 86% of the Madera brachiopods are well preserved in their original mineralogy, microstructure and geochemistry. In contrast, cements and matrix have undergone extensive post-depositional alteration. It is confirmed that brachiopods are superior to cements/matrix in defining depositional parameters by using their geochemistry.

c) No biogenic fractionation or vital effects are observed on the shell secretion of the Madera brachiopods, at least for Composita and Neospirifer. Such conclusion is not only ascertained by temporal and spatial analyses of the $\delta^{18}O$ and $\delta^{13}C$ compositions, but also strongly supported by student's *t*-test.

d) In a paleoenvironmental context, the Jemez Springs section is closer to the Penasco Uplift; sea water is more aerobic, and the water chemistry is more influenced by continental sources than those at Battleship Rock. In contrast, the latter has undergone stronger dolomitization.

ACKNOWLEDGMENTS

I am deeply indebted to my thesis supervisor, Professor Dr. Uwe Brand (Brock University & McMaster University), for his elaborate training, continual encouragement, and providing samples. I would like to say "thank you" to him in a Chinese way, which means a lot.

Dr. Peter von Bitter, Department of Invertebrate Paleontology, Royal Ontario Museum is thanked for conodont identifications. Mr. Bill Parkins is thanked for conodont sample preparation.

Special thanks go to Dr. Steve Westrop, for his reading and discussion of this thesis. To Dr. Francine McCarthy, who introduced me to paleoclimatology.

My gratitude goes to Howard Melville for his assistance with the SEM, and to Mike Lozon, for his advice and help in preparation of figures. I further extend my gratitude to Brian Grant and Anne Sawchuk of this department, for their friendship and everyday help.

I would also like to thank my family, my wife Guoqing Lin and my daughter Jie, for their understanding, tolerance and love, especially in the tough economic time.

During the two years' study at Brock University, financial support from the Ontario Graduate Scholarship is gratefully acknowledged.

REFERENCES CITED

Adams, A.E., MacKenzie, W.S. & Guilford, C., 1984, Atlas of sedimentary rocks under the microscope, John Wiley & Sons, 104p.

Adlis, D.S., Grossman, E.L., Yancey, T.E. & McLerran, R.D.,1988, Isotope stratigraphy and paleodepth changes of Pennsylvanian cyclical sedimentary deposits, Palaios, **3**, 487-506.

Al-Aasm, I.S. & Veizer, J., 1982, Chemical stabilization of low-Mg calcite: An example of brachiopods, J. Sediment. Petrol., **52**, 1101-1109.

Armstrong, A.K., 1962, Stratigraphy and paleontology of the Mississippian System in southwestern New Mexico and adjacent southeastern Arizona: New Mexico Bur. Mines & Miner. Res. Mem. 8, 99p.

Armstrong, A.K., Kottlowski, F.E., Stewart, W.J., Mamet, B.L., Baltz, E.H., Siemers, W.T. & Thompson, S. III, 1979, The Mississippian and Pennsylvanian (Carboniferous) Systems in the United States - New Mexico, in Avcin, M.J. & Koch, D.L. eds., The Mississippian and Pennsylvanian (Carboniferous) Systems in the United States, Geol. Surv. Prof. Paper 1110-M, W1-W27.

Arthur, M.A., Anderson, T.F., Kaplan, I.R., Veizer, J & Land, L.S., 1983, Stable isotopes in sedimentary geology, SEPM Short Course 10, 432p.

Bachman, G.O., 1953, Geology of a part of northwestern Mora County, New Mexico, U.S. Geol. Surv. Oil and Gas Inv. Map, OM-137.

Bachman, G.O. & Dane, C.H., 1962, Preliminary geological map of the northeastern part of New Mexico, U.S. Geol. Surv. Misc. Geol. Inv. map, I-358.

Bachman, G.O. & Hayes, D.A., 1975, The Lead Camp Limestone and its correlatives in south-central New Mexico, New Mexico Geol. Soc. Guidebook, 26th Field Conf., 105-108.

Baker, P.A., Gieskes, J.M. & Elderfield, H., 1982, Diagenesis of carbonates in deep sea sediments- Evidence from Sr/Ca ratios and interstitial Sr data, J. Sediment. Petrol., **52**, 71-82.

Baltz, E.H., 1972, Geologic map and cross sections of the Gallinas Creek area, Sangre de Cristo Mountains, New Mexico, U.S. Geol. Surv. Misc. Geol. Inv. Map, I-673.

Baltz, E.H. & Bachman, G.O., 1956, Notes on the geology of the southern Sangre de Cristo Mountains, New Mexico, New Mexico Geol. Soc. Guidebook, 7th Field Conf., 96-108.

Bates, N.R., 1989, Biogeochemistry of Paleozoic brachiopods from New York state and Ontario, Unpublished M.Sc. thesis, Brock University, 257p.

Bates, N.R. & Brand, U., 1991, Environmental and physiological influences on isotopic and elemental compositions of brachiopod shell calcite: Implications for the isotopic evolution of Paleozoic oceans, Chem. Geol., **94**, 67-78.

Bathurst, R.G.C., 1976, Carbonate sediments and their diagenesis, Elsevier, 658p.

Bennett, R.H., Bryant, W.R. & Keller, G.H., 1977, Clay fabric and geotechnical properties of selected submarine sediment cores from the Mississippi delta, NOAA Prof. Paper 9, U.S. Dept. of Commerce, NOAA/ERL, 86p.

Bennett, R.H. & Hulbert, M.H., 1986, Clay microstructure, International Human Resources Development Corporation Press, Printice Hall, MA, 161p.

Bennett, R.H., O'Brien, N.R. & Hulbert, M.H., 1991, Determinants of clay and shale microfabric signatures: Processes and mechanisms, in Bennett, R.H., Bryant, W.R. & Hulbert, M.H. eds., Microstructure of Fine-Grained Sediments: From Mud to Shale, Springer-Verlag, 5-32.

Brand, U., 1981, Mineralogy and chemistry of the lower Pennsylvanian Kendrick fauna, eastern Kentucky-1: Trace elements, Chem. Geol., **32**, 1-16.

Brand, U., 1982, The oxygen and carbon isotope composition of Carboniferous fossil components: Seawater effects, Sedimentology, **29**, 139-147.

Brand, U., 1983, Mineralogy and chemistry of the lower Pennsylvanian Kendrick fauna, eastern Kentucky, USA, Chem. Geol., **40**, 167-181.

Brand, U., 1987, Biogeochemistry of nautiloids and paleoenvironmental conditions of Buckhorn seawater (Pennsylvanian), southern Oklahoma, Paleogeog. Paleoclim. Paleoecol., **61**, 255-264.

Brand, U., 1989, Aragonite-calcite transformation based on Pennsylvanian molluscs, Geol. Soc. Am. Bull., **101**, 377-390.

Brand, U., 1989, Biogeochemistry of Late Paleozoic North American brachiopods and secular variation of seawater composition, Biogeochemistry, **7**, 159-193.

Brand, U., 1989, Global climatic changes during the Devonian-Mississippian: Stable isotope biogeochemistry of brachiopods, Paleogeog. Paleoclim. Paleoecol., **75**, 311-329.

Brand, U., 1990, Chemical diagenesis and dolomitization of Paleozoic high-Mg calcite crinoids, Carbonates and Evaporates, **5**, 179-195.

Brand, U., 1991, Strontium isotope diagenesis of biogenic aragonite and low-Mg calcite, Geochim. Cosmochim. Acta, **55**, 505-513.

Brand, U., 1994, Morphochemical and replacement diagenesis of biogenic carbonates, in Wolf, K.H. & Chilingarian, G.V. eds., Diagenesis, IV, Developments in Sedimentology 51, Elsevier, 217-282.

Brand, U. & Logan, A., 1991, Brachiopod geochemistry: A tracer tool of present and past ocean circulation, chemistry and cycles, Joint Annual Meeting GAC/MAC, Program with Abstracts, **16**, A14.

Brand, U. & Morrison, J.O., 1987, Diagenesis and pyritization of crinoid ossicles, Can. J. Earth Sci., **24**, 2486-2498.

Brand, U. & Morrison, J.O., 1987, Paleoscence No.6, Biogeochemistry of fossil marine invertebrates, Geosci. Can., **14**, 85-107.

Brand, U. & Veizer, J., 1980, Chemical diagenesis of a multicomponent carbonate system-1: Trace elements, J. Sediment. Petrol., **50**, 1219-1236.

Brand, U. & Veizer, J., 1981, Chemical diagenesis of a multicomponent carbonate system-2: Stable isotopes, J. Sediment. Petrol., **51**, 987-997.

Brill, K.G., 1952, Stratigraphy in the Permo-Pennsylvanian zeugogeosyncline of Colorado and northern New Mexico, Geol. Soc. Am. Bull., **63**, 809-880.

Broecker, W.S. & Peng, T.-H., 1982, Tracers in the sea, a Publication of the Lamont-Doherty Geological Observatory, Columbia University, 690p.

Carpenter, S.J., Lohmann, K.C., Holden, P., Walter, L.M., Huston, T.J. & Halliday, A.N., 1991, ^{18}O values, $^{87}Sr/^{86}Sr$ and Sr/Mg ratios of Late Devonian abiotic marine calcite: Implications for the composition of ancient seawater, Geochim. Cosmochim. Acta, **55**, 1991-2010.

Casey, J.M., 1980, Depositional systems and paleogeographic evolution of the Late Paleozoic Taos Trough, northern New Mexico, in Fouch, T.D. & Magathan, E.R. eds., Paleozoic Paleogeography of west-central United States, Rocky Mountain Section, Denver, Colorado, 181-196.

Chave, K.E., 1954, Aspects of the biochemistry of magnesium, 1. Calcareous and marine organisms, J. Geol., **62**, 266-283.

Craig, H.,1957, Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide, Geochim. Cosmochim. Acta, **12**, 133-149.

Craig, H., 1961, Standards for reporting concentrations of deuterium and oxygen-18 in natural waters, Science, **133**, 1833-1834.

Craig, H., 1965, The measurement of oxygen isotope paleotemperatures, in Tongiorgi, E. ed., Stable Isotopes in Oceanographic Studies and Paleotemperatures, Consiglio Nazionale Richerche, Lab. Geol. Nucleare: Pisa, 161-182.

Dunham, R.J., 1962, Classification of carbonate rocks according to depositional texture, in Ham, W.E., ed., Classification of Carbonate Rocks, AAPG Mem. 1,108-121.

Epstein, S., Buchsbaum, R., Lowenstam, H.A. & Urey, H.C., 1953, Revised carbonate-water isotopic temperature scale, Geol. Soc. Am. Bull., **64**, 1315-1326.

Erez, J., 1978, Vital effect on stable isotope composition seen in foraminifera and coral skeletons, Nature, **273**, 199-202.

Faure, G., 1986, Principles of isotope geology, John Wiley & Sons, 589p.

Faure, G., 1991, Principles and applications of inorganic geochemistry, Macmillan, 626p.

Folk, R.L., 1962, Spectral subdivision of limestone types, in Ham, W.E., ed., Classification of Carbonate Rocks, AAPG Mem. 1, 62-84.

Friedman, I. & O'Neil, J.R., 1977, Compilation of stable isotope fractionation factors of geochemical interest, in Fleischer, M. ed., Data of Geochemistry, U.S. Geol. Surv. Prof. Paper 440.

Fritz, P. & Poplawski, S., 1974, ^{18}O and ^{13}C in the shells of fresh-water molluscs and their environments, Earth Planet. Sci. Lett., **24**, 91-98.

Fursich, F.T. & Hurst, J.M., 1974, Environmental factors determining the distribution of brachiopods, Paleontology, **17**, 879-900.

Gehrig, J.L., 1958, Middle Pennsylvanian brachiopods from the Mud Springs Mountains and Derry Hills, New Mexico, New Mexico Bur. Mines and Miner. Res. Mem. 3, 24p.

Given, R.K. & Lohmann, K.C., 1985, Derivation of the original isotopic compositions of Permian marine cements, J. Sediment. Petrol., **55**, 430-439.

Gordon, C.H., 1907, Notes on the Pennsylvanian formations in the Rio Grande Valley, New Mexico, J. Geol., **15**, 805-816.

Gordon, L. Salutsky, M.L. & Willard, H.H., 1959, Precipitation from homogenous solution, Wiley, 289p.

Grossman, E.L., MII, H.S. & Yancey, T.E., 1993, Stable isotopes in Late Pennsylvanian brachiopods from the United States: Implications for Carboniferous paleoceanography, Geol. Soc. Am. Bull., **105**, 1284-1296.

Harris, D.C., 1991, Quantitative chemical analysis, Third Edition, Freeman and Company, 782p.

Harland, W.B., Armstrong, R.L., Craig, L.E., Smith, A.G. & Smith, D.G., 1990, A geological time scale 1989, Cambridge University Press, 263p.

Hecht, A.D., 1985, Paleoclimatology: A retrospective of the past 20 years, in Hecht, A.D. ed., Paleoclimate analysis and modeling, Wiley-Interscience, 1-25.

Karhu, J. & Epstein, S., 1986, The implication of the oxygen isotope records in coexisting cherts and phosphates, Geochim. Cosmochim. Acta, **50**,1745-1756.

Kim, Jae-On, 1975, Factor analysis, in Nie, N.H., Hull, C.H., Jenkins, J.G., Steinbrenner, K. & Bent, D.H. eds., Statistical Package for the Social Sciences (SPSS), Second Edition, McGraw-Hill, 675p.

Lepzelter, C.G., Anderson, T.F. & Sandberg, P.A., 1983, Stable isotope variation in modern articulate brachiopods (abs.), Am. Asso. Petro. Geol. Bull., **67**, 500-501.

Lindholm, R.C. & Finkelman, R.B., 1972, Calcite staining: semiquantitative determination of ferrous iron, J. Sediment. Petrol., **42**, 239-242.

Lohmann, K.C. & Meyers, W.J., 1977, Microdolomite inclusions in cloudy prismatic calcites: A proposed criterion for former high-magnesium calcites, J. Sediment. Petrol., **47**, 1078-1088.

Lowenstam, H.A., 1961, Mineralogy, $^{18}O/^{16}O$ ratios, and strontium and magnesium contents of Recent and fossil brachiopods and their bearing on the history of the oceans, J. Geol., **69**, 241-260.

Lowenstam, H.A., 1964, Paleotemperatures of the Permian and Cretaceous Periods, in Nairn, A. E. M. ed., Problems in Paleoclimatology, Interscience, London, 227-248.

Lowenstam, H.A. & Epstein, S., 1954, Paleotemperatures of the post-Aptian Cretaceous as determined by the oxygen isotope method, J. Geol., **62**, 207-248.

Luz, B., Kolodny, Y. & Kovach, J., 1984, Oxygen isotope variations in phosphate of biogenic apatites-3: Conodonts, Earth Plan. Sci. Lett., **69**, 255-262.

McConnaughey, T., 1989, ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates, I: Patterns, Geochim. Cosmochim. Acta, **53**, 151-162.

McConnaughey, T., 1989, ^{13}C and ^{18}O isotopic disequilibrium in biological carbonates, II: In vitro simulation of kinetic isotope effects, Geochim. Cosmochim. Acta, **53**, 163-171.

McCrea, J.M., 1950, On the isotopic chemistry of carbonates and a paleotemperature scale, J. Chem. Phys., **18**, 849-857.

McIntire, W.L., 1963, Trace element partition coefficients: A review of theory applications to geology, Geochim. Cosmochim. Acta, **27**, 1209-1264.

Milliman, J.D., 1974, Marine carbonates, Springer-Verlag, 375p.

Morrison, J.O., Molluscan carbonate geochemistry and paleoceanography of the Late Cretaceous western interior seaway of North America, Unpublished M.Sc. thesis, Brock University, 214p.

Morrison, J.O., Brand, U. & Rollins, H.R., 1985, Paleoenvironmental and chemical analysis of the Pennsylvanian Brush Creek fossil allochems, Pennsylvanian, USA, 10th International Carboniferous Congress, Madrid, Compte Rendu (Madrid), 2, 271-280.

Morse, J.W. & Mackenzie, F.T., 1990, Geochemistry of sedimentary carbonates, Elsevier, 707p.

Mukhopadhyay, B. & Brookins, D.G., 1976, Rb-Sr whole rock geochronology and clay mineralogy of the Madera Formation near Albuquerque, New Mexico, J. Sediment. Petrol., **46**, 680-688.

Mukhopadhyay, B. & Brookins, D.G., 1976, Strontium isotopic composition of the Madera Formation (Pennsylvanian) near Albuquerque, New Mexico, Geochim. Cosmochim. Acta, **40**, 611-616.

O'Neil, J.R., 1987, Preservation of H, C and O isotopic ratios in the low temperature environment, in Kyser, T.K. ed., Stable Isotope Geochemistry of Low Temperature Fluids, MAC Short Course 13, 85-128.

O'Neil, J.R. & Epstein, S., 1966, Oxygen isotope fractionation in the system dolomite-calcite-carbon dioxide, Science, **152**, 198-201.

Popp, B.N., Anderson, T.F. & Sandberg, P.A., 1986, Textural, elemental and isotopic variations among constituents in Middle Devonian limestones, North America, J. Sediment. Petrol., **56**, 715-727.

Popp, B.N., Anderson, T.F. & Sandberg, P.A., 1986, Brachiopods as indicators of original isotopic compositions in some Paleozoic limestones, Geol. Soc. Am. Bull., **97**, 1262-1269.

Pratt, L.M., 1993, Frontiers in sedimentary geology, J. Sediment. Petrol., **63**, 181-182.

Read, C.B. & Wood, G.H. Jr., 1947, Distribution and correlation of Pennsylvanian rocks in Late Paleozoic sedimentary basins of northern New Mexico, J. Geol., **55**, 220-236.

Roberts, J.W., Barnes, J.J. & Wacker, H.J., 1976, Subsurface Paleozoic stratigraphy of the northeastern New Mexico basin and arch complex, in Ewing, R.C. & Kues, B.S. eds., New Mexico Geol. Soc. Guidebook, 27th Field Conf., 141-152.

Rohlf, F.J. & Sokal, R.R., 1981, Statistical Tables, Second Edition, Freeman and Company, 219p.

Rosenbaum, J.M., 1993, Room temperature oxygen isotope exchange between liquid CO_2 and H_2O, Geochim. Cosmochim. Acta, **57**, 3195-3198.

Rush, P.F. & Chafetz, H.S., 1990, Fabric-retentive non-luminescent brachiopods as indicators of original $\delta^{13}C$ and $\delta^{18}O$ composition: A test, J. Sediment. Petrol., **60**, 968-981.

Schidlowski, M., 1986, $^{13}C/^{12}C$ ratios as indicators of biogenicity, in Johns, R.B. ed., Biological markers in the sedimentary record, Elsevier, 347-361.

Scoffin, T.P., 1987, An introduction to carbonate sediments and rocks, Blackie & Son, 274p.

Shackleton, N.J., 1987, Oxygen isotope, ice volume and sea level, Quat. Res., **6**, 183-190.

Sokal, R.R. & Rohlf, F.J., 1981, Biometry, Second Edition, Freeman and Company, 859p.

Sutherland, P.K., 1963, Paleozoic rocks, in Miller, J.P., Montgomery, Arthur & Sutherland, P.K. eds., Geology of the Southern Sangre de Cristo Mountains, New Mexico, New Mexico Bur. Mines & Miner. Res. Mem. 11, 22-46.

Sutherland, P.K. & Harlow, F.H., 1967, Late Pennsylvanian brachiopods from north-central New Mexico, J. Paleont., **41**, 1065-1089.

Sutherland, P.K. & Harlow, F.H., 1973, Pennsylvanian brachiopods and biostratigraphy in southern Sangre de Cristo Mountains, New Mexico, New Mexico Bur. Mines and Mineral Resources mem. 27, 173p.

Trewin, N., 1988, Use of the scanning electron microscope in sedimentology, in Tucker, M. ed., Techniques in Sedimentology, Blackwell Sci. Publ., 229-273.

Urey, H.C., 1947, The thermodynamic properties of isotopic substances, J. Chem. Soc., 562-581.

Urey, H.C., 1948, Oxygen isotope in nature and in the laboratory, Science, **108**, 489-496.

Usdowski, E. & Hoefs, J., 1993, Oxygen isotope exchange between carbonic acid, bicarbonate, carbonate, and water: A re-examination of the data of McCrea (1950) and an expression for the overall partitioning of oxygen isotopes between the carbonate species and water, Geochim. Cosmochim. Acta, **57**, 3815-3818.

Veizer, J., 1983, Chemical diagenesis of carbonates: Theory and application of trace element techniques, Stable Isotopes in Sedimentary Geology, SEPM Short Course 10, 3.1-3.100.

Veizer, J., 1983, Trace elements and isotopes in sedimentary carbonates, in Reeder, R. J. ed., Carbonates: mineralogy and Chemistry, Reviews in Mineralogy 11, 265-300.

Veizer, J. & Demovic, R., 1974, Strontium as a tool in facies analysis, J. Sediment. Petrol., **44**, 93-115.

Veizer, J., Fritz, P. & Jones, B., 1986, Geochemistry of brachiopods: Oxygen and carbon isotopic records of Paleozoic oceans, Geochim. Cosmochim. Acta, **50**, 1679-1696.

Veizer, J., Lemieux, J., Jones, B., Gibling, M.R. & Savelle, J., 1978, Paleosalinity and dolomitization of a lower Paleozoic carbonate sequence, Somerset and Prince of Wales Islands, Arctic Canada, Can. J. Earth Sci., **15**, 1448-1461.

Weber, J.N. & Woodhead, P.M.J., 1970, Carbon and oxygen isotope fractionation in the skeletal carbonate of reef-building corals, Chem. Geol., **6**, 93-117.

Woo, K.S., Anderson, T.F. & Sandberg, P.A., 1993, Diagenesis of skeletal components of Mid-Cretaceous limestones, J. Sediment. Petrol., **63**, 18-32.

APPENDIX I

DATA OF TRACE ELEMENT ANALYSIS, MADERA FORMATION, NEW MEXICO

SAMPLE	SP[1]	IR[2]	Ca	Mg	Sr	Na	Fe	Mn	Zn	Cd[3]
UL -1A	1	20.6	325382	2099	287	2129	358	364	0	1419
-1B	2	29.6	302410	1299	423	1241	951	164	0	345
-1BM	6	80.2	317284	2407	219	5630	582	1344	52	1177
-1C	2	20.1	355047	2896	592	1030	105	289	0	545
-2A1	4	17.3	308333	2009	469	1616	100	129	8	675
-2A2	4	14.9	360138	1895	582	1453	102	115	12	659
-2B	1	16.5	326923	940	353	1421	121	667	5	290
-2BM1	6		342786	796	272	1035	264	1407	4	269
-2BM2	6	17.1	308638	630	175	1278	231	1256	7	272
-2C	1	16.1	391157	837	441	1818	26	119	5	72
-2E	2	15.5	393262	793	613	2010	66	194	2	146
-2EM1	6	25.2	328176	1333	267	1445	161	684	9	967
-2EM2	6	28.0	346910	1563	270	1492	192	820	8	1141
-2F	2	56.1	400184	1812	390	9850	263	1142	35	399
-4A	1	18.8	279333	1638	402	1540	76	279	7	714
-4B	1	16.8			397	1565	60	554	5	837
-4BM1	6	5.3	333713	1050	312	1057	153	1422	4	1005
-4BM2	6	15.2	269132	1085	312	1248	152	1506	5	1021
-4C	1	20.7	384324	1343	386	1653	87	330	4	249
-4D1	2	15.1	330076	948	620	2086	31	58	2	68
-4D2	2	16.7	380981	954	690	2262	30	30	1	54
-4DM1	6	25.9	294000	2900	460	1493	259	377	24	1065
-4DM2	6	25.7	379458	2824	454	1476	277	409	21	1048
-4E	2	16.4	335419	2525	491	1754	311	442	26	1000
-4F	1	46.8	379717	1769	399	2142	111	383	17	1159
UL -4FM1	6	16.0	369718	719	139	1229	363		2	209
-4FM2	6	15.1	387069	706	132	1194	371		1	143
-4G1	2	28.1	339346	1174	522	2012	111	561	6	468
-4G2	2	19.7	355972	727	603	1977	31	94	1	158
-4GM1	6	20.5	352402	2544	372	1425	362	677	19	1264
-4GM2	6	22.2	371179	2324	342	1354	391	706	17	1305
-4H1	1	16.2	376033	900	433	1836	77	193	5	231
-4H2	1	7.9	377846	1092	425	1794	67	225	6	315
-4I	1	8.2	406367	1279	385	1412	37	123	4	335
-5A	1	9.4	432172	1107	426	1279	94	359	6	402
-5AM	6	4.8	407436	771	295	1055	345	1554	7	518
-5B	2	12.6	398369	1369	562	2015	126	282	15	425
-6A	1	18.8	347945	1667	386	1191	116	230	19	653
-6AM	6		425147	1223	339	966	321	1009	7	688
-6B1	2	12.8	369824	908	706	2138	50	93	9	67
-6B2	2	13.8	390105	998	699	2093	37	50	2	161
-6BM	6	51.7	352434	5096	372	2480	1140	701	35	5324
-6C1	2	13.8	381392	1065	653	2224	64	78	3	111
-6C2	2	23.2	373193	1910	557	2134	290	465	10	824
MMA-1	1	1.8	381696	1116	359	1075	46	433	3	349
-1S	5	10.3	386213	927	329	1265	133	971	0	326
-1M1	6	11.1	395475	1749	311	1227	113	804	3	575
-1M2	6	11.4	411251	1802	315	1283	118	808	4	579
-2	1	10.0	340613	868	453	1560	88	435	2	492
-3	2	3.2	451923	2552	456	1122	152	273	9	362

SAMPLE	SP	IR	Ca	Mg	Sr	Na	Fe	Mn	Zn	Cd
MMA -4A	3	8.9	323950	1933	406	1538	47	75	7	217
-4B	3	8.4	384718	1971	437	1584	45	80	7	260
-4M1	6	19.5	364150	1452	217	1342	227	610	5	502
-4M2	6	17.2	370338	1471	206	1308	247	643	3	496
-5	1	9.5	368817	1008	322	1411	53	448	5	157
-5S	5	10.2	360705	989	203	1238	60	1090	2	233
-6	1	10.3	374932	1018	322	1312	56	537	2	337
-6S	5	8.8	385277	860	283	1147	99	982	1	285
-7	1	2.6	417882	1883	464	1203	48	127	5	217
-7M	6	36.3	351278	2053	312	1789	501	612	9	573
-8-1	1	1.2	386792	1664	556	1507	53	75	12	229
-8-2	1	12.2	389848	1594	579	1706	48	65	7	247
-9	1	10.5	396930	1768	538	1680	73	98	5	238
-10	3	15.3	375431	1937	692	1817	84	155	7	336
-10M1	6	29.1	337908	2033	589	1807	213	259	46	1006
-10M2	6	25.4	325908	2244	425	178	165	253	2	791
-11	3	4.8	305114	2266	936	617	50	124	0	306
-12A	7	17.5	335827	968	584	804	18	36	0	145
-12B1	7	17.7	336243	978	593	858	67	20	0	41
-12B2	7	17.4	346831	1056	587	904	174	22	0	46
-13	1	7.8	345663	1664	413	808	170	116	4	264
-14A	2	5.8	320169	1198	592	1159	136	45	0	91
-14B	2	12.5	385375	1637	482	844	325	83	0	272
-14M1	6	26.0	259819	2209	267	80	157	173	3	532
-14M2	6	23.1	328174	3064	324	131	376	238	5	585
MMA-15-1	2	14.4	337752	893	506	1210	98	27	32	29
-15-2	2	12.1	270023	677	561	1038	33	19	43	58
-19	2	6.9	321071	1846	572	1395	502	110	75	231
UL-20	2	5.8	309575	1061	494	683	368	33	94	74
-21M1	6	68.6	301092	7137	434	421	1829	563	76	272
-21M2	6	14.2	352038	1033	557	1002	37	11	57	26
-22	2	14.7	340311	1092	602	1056	136	14	57	49
-23	1	9.3	339666	1151	451	976	74	35	43	84
-24M1	6	29.9	228893	2326	212	134	279	675	59	506
-24M2	6	29.6	298249	3228	263	175	588	1007	69	492
-25M1	6	19.0	326406	2347	732	126	444	531	56	150
-25M2	6	18.9	332938	2522	786	134	911	545	36	106
-26	3	7.4	401667	2533	1056	98	180	139	47	
-27M	6	13.2	322911	1840	639	94	317	284	17	219
-30M1	6	26.8	317955	1682	406	87	429	375	31	132
-30M2	6	26.0	311642	1602	381	92	421	376	35	137
-31	1	6.9	297044	1515	593	1000	290	119	57	58
-32	3	24.0	296414	3112	523	649	182	253	28	64
-33M	6	10.3	352981	1951	368	62	330	381	26	99
-34A	2	5.0	342733	1574	724	892	523	116	25	65
-34B	2	9.2	342615	1554	723	1046	96	51	41	52
-35M1	6	16.6	347149	1705	892	135	386	146	31	223
-35M2	6	18.3	317193	1520	918	134	235	142	27	186
BR -1	1	15.3	328687	1802	264	62	172		23	
-2	3	13.2	321086	2055	298	258	259	732	26	325

SAMPLE	SP	IR	Ca	Mg	Sr	Na	Fe	Mn	Zn	Cd
BR -3	7	8.6	406810	.2658	421	86	556	651	26	
-4	5	12.3	317509	2389	414	99	314	939	30	419
-5	1	16.2	269435	1090	353	514	82	79	19	
-6	7	14.5	300982	1385	372	554	80	58	20	40
-7	7	18.8	336237	1093	527	765	45	35	28	133
-8M1	6	34.6	345194	2887	163	160	409	778	14	351
-8M2	6	35.1	335622	2899	231	179	439	820	14	366
-9	1	10.4	348485	2006	447	946	79	88	7	131
-10	1	9.9	331090	2773	568	1011	217	115	7	
-11A	1	8.4	333598	1908	596	972	135	70	9	86
-11B	1		373490	1704	563	1097	81	40	6	51
-12	2	10.4	333831	4050	787	219	361	351	9	582
-13	1		344250	1075	433	625	38	31	3	51
-14A	1	10.2	345455	1378	487	1014	58	68	6	141
-14B	1	9.0	347861	1257	509	1045	55	42	5	133
-15-1	5	15.8	347525	4935	552	156	561	428	9	1088
-15-2	5	14.9	340634	4885	560	153	623	466	9	580
-16	5		323985	2649	513	37	620	932	5	241
-17-1	2	10.9	286711	907	599	969	45	60	4	38
-17-2	2	11.4	334216	1004	608	945	30	24	4	26
-18	4	10.6	341259	6803	771	228	2353	792	6	54
-19A	1	12.3	333729	1971	564	913	234	169	6	92
-19B	1		333739	998	416	655	52	30	5	46
-20	1	9.9	335127	1780	466	889	78	142	5	116
-20S	5		325987	1541	202	43	417	1580	4	71
BR-21	1	4.9	332208	1748	448	547	170	208	10	212
-22A	2	10.5	345953	950	598	920	73	76	6	43
-22B	2	10.9	336832	968	592	875	51	69	5	40
-22C	2	9.3	346144	2009	571	1020	121	115	7	112
-23	1	4.5	294638	2272	505	1027	291	201	3	308
-23S1	5	3.6	318406	8437	613	127	412	392	40	651
-23S2	5	3.5	342642	8788	620	135	417	403	12	598
-24	2	3.0	370349	1443	551	585	88	80	5	82
-24M	6	8.3	352742	2959	558	171	382	374	10	202
-25A	1	6.2	314918	1404	586	964	110	79	4	64
-25B	1	1.7	319131	1637	625	1245	88	61	25	51
-26	3	10.3	309530	2528	697	837	157	98	19	450
-26M1	6	30.2	290809	2960	537	239	403	464	8	3396
-26M2	6	30.7	302853	2999	498	212	422	494	32	1515
-27	3	37.0	325000	3049	663	699	215	129	15	248
-27M	6	8.9	328176	3176	469	140	298	321	9	651
-28	3	31.7	347703	3464	780	821	135	323	30	660
-28M1	6	36.6	211518	2459	459	142	851	504	8	877
-28M2	6	36.6	330437	3698	681	243	1334	786	13	1289
-29A	3	11.9	360821	3062	738	832	385	946	14	1009
-29B	3	7.3	323721	3022	737	1615	316	1045	37	972
-29C	3	22.7	309347	3024	808	873	358	544	12	541
-29D	3	34.1	307582	2930	753	898	406	384	11	427
-29M1	6	14.1	315909	3565	403	193	531	731	15	507
-29M2	6	15.9	329176	3785	440	154	600	404	16	588

SAMPLE	SP	IR	Ca	Mg	Sr	Na	Fe	Mn	Zn	Cd
BR-30M1	6	10.2	346240	4321	561	244	379	308	13	496
-30M2	6	11.7	355225	4320	573	234	370	300	11	482
-31	3	6.4	330567	2088	758	450	216	170	11	218
-32M1	6	14.9	312426	17959	1064	246	1118	338	14	599
-32M2	6	15.0	281467	17754	1069	225	1167	340	14	588
-33	3	7.0	278206	4830	881	514	378	129	10	236
-34A	3	6.4	340676	4284	905	616	491	131	10	402
-34B	3	10.4	301152	7167	930	694	912	223	21	530
-34M	6	17.9	317284	12394	929	194	1751	384	13	1028
-34M'1	6	17.8	337469	13036	954	196	1769	388	16	1030
-34M'2	6	17.9	331920	13098	965	209	1787	391	41	930
-35A	3	13.5	355271	3298	762	786	457	119	11	552
-35B	3	13.4	316176	4015	869	579	530	158	10	744
-35C1	3	13.2	280488	4453	887	587	548	167	11	784
-35C2	3	13.7	320299	4715	871	579	545	164	10	811
-36	3	13.0	315872	3819	1323	468	332	103	11	453
-36M1	6	19.4	280384	7195	1185	211	813	226	14	511
-36M2	6	20.1	339308	7715	1172	165	838	232	14	525
-36M'	6	20.2	354864	7786	1212	208	830	232	14	605
-37	4	12.2	284064	4781	1157	181	364	424	12	394
-38	1	14.1	324929	4020	957	797	615	174	36	513
-39	1	11.4	340770	2476	717	1247	326	63	32	233
-40	1	10.7	352771	1299	600	745	145	24	9	59
-40M1	6	36.0	332738	20456	945	425	2493	374	20	595
-40M2	6	36.8	335857	20518	950	339	2619	393	19	592
BR-40M'	6	39.0	349492	23137	851	402	3009	447	19	557
-41A	2	13.2	348598	1703	675	1291	336	58	15	105
-41B	2	23.1	340153	4060	900	930	620	129	26	336
-41M	6	50.6	352808	13064	1194	582	1537	284	27	708
-41M'1	6	49.7	322548	9985	1055	389	1374	265	17	428
-41M'2	6	52.0	366146	11380	1193	458	1512	291	18	476
-42	3	27.6	350913	3296	801	1129	642	212	69	415
-43	2	11.7	341772	1870	794	1372	220	40	11	393
-44	2									
-45	1	23.0	274685	3082	769	1037	509	105	20	306
-46A	2	7.8	303850	1050	733	942	165	20	7	73
-46B	2	24.5	359109	2277	755	1055	380	65	7	181
-46M1	6	66.7	373083	11771	679	997	2307	536	31	1729
-46M2	6	67.6	355978	11801	589	963	2424	564	33	1819
-47A1	3	14.9	340133	4138	1037	179	226	283	20	18801
-47A2	3	15.0	338924	4121	1092	197	178	278	19	18271
-47B	3	15.8	314663	3255	861	836	367	159	20	893
-47C	3	9.6	375284	3732	815	551	221	235	15	2656
-47M	6	35.1	355534	9032	797	538	1448	382	11	684
-47M'1	6	41.7	355536	9018	724	523	1428	380	9	558
-47M'2	6	44.4	349819	9211	739	413	1482	396	30	621
-48A	3	17.4	370456	3635	840	1017	420	103	24	290
-48B	3	16.6	350123	3112	822	995	322	67	24	152
-48M1	6	55.8	287640	9579	824	1236	1641	493	38	713
-48M2	6	55.4	300434	9734	738	1123	1635	499	36	785

SAMPLE	SP	IR	Ca	Mg	Sr	Na	Fe	Mn	Zn	Cd
BR-48M'	6	56.4	276825	10288	652	780	2101	548	36	708
-49A1	4	13.6	360946	6469	671	274	458	154	17	267
-49A2	4	12.2	345497	6151	654	218	400	124	4	216
-49B	4	12.5	360921	6947	725	249	468	111	3	205
-50	2	6.9	340811	905	682	619	68	9	1	14
-51M	6	64.7	344421	12840	772	1352	1968	536	9	873
-51M'1	6	64.8	309655	12862	694	1538	2105	567	9	958
-51M'2	6	62.5	287109	11784	623	1315	1987	533	8	936
-52A1	2	14.0	347989	1696	638	732	296	103	2	140
-52A2	2	12.6	366667	1770	666	867	252	90	2	91
-52B	2	12.3	316310	1757	662	736	217	27	3	78
-52M1	6	48.1	347966	11979	712	372	1583	461	8	913
-52M2	6	49.5	352897	12188	672	539	1775	484	11	939
-52M'	6	47.4	306663	10676	686	428	1581	456	11	954
-53A	1	13.1	336087	3261	652	617	330	269	7	1100
-53B	1	5.7	351274	1722	615	754	183	59	7	334
-54	2	20.5	335374	4222	758	744	877	254	9	218
-55A	3	7.8	306670	2603	779	922	194	40	7	67
-55B1	3	20.3	363866	4264	742	853	828	319	12	283
-55B2	3	19.3	362555	4280	746	840	906	345	12	307
-55C	3	13.3	296986	3388	750	1086	667	201	15	226
-55M1	6	34.6	308614	5974	500	228	1511	668	7	161
-55M2	6	36.0	315860	6644	440	246	1696	747	6	175
-55M'	6	37.6	329787	7160	465	200	1748	728	8	281
-56	1	25.7	366376	2997	493	732	819	351	8	20772
BR-57	1	6.7	339920	889	451	732	137	26	5	91
-57M	6	11.8	337271	5586	599	156	643	345	11	968
-57M'1	6	13.7	313584	5867	626	176	879	404	11	1062
-57M'2	6	14.0	361095	6077	621	135	883	400	8	340
-58	3	11.2	303016	2377	502	622	280	82	8	308
-59-1	4	13.3	329753	6210	579	227	262	230	5	123
-59-2	4	12.3	358739	6160	584	295	262	237	2	111
-60	4	14.7	356934	5164	842	275	1040	515	18	1185
-61A	2	10.3	369789	1153	696	748	147	41	6	18
-61B	2	9.4	368620	1304	690	808	124	32	7	0
-62	1	15.3	358869	3167	669	810	464	154	11	443
-62M1	6	21.9	318079	5336	564	194	887	529	14	965
-62M2	6	21.8	340689	5428	552	222	809	550	14	899
-62M'	6	15.1	370365	5293	569	173	638	339	15	962
-63	3	15.1	371230	3282	866	704	345	136	18	912
-64A	2	13.8	346038	1921	717	774	305	98	11	95
-64B	2	16.1	302813	2184	665	781	340	98	12	92
-65	2	10.8	291452	1592	693	780	152	36	4	42
-65M1	6	45.7	321753	10876	693	359	1420	481	10	688
-65M2	6	44.8	340229	10739	651	383	1502	505	11	406
-65M'	6	51.1	279088	12107	642	456	1619	499	14	836
-66	4	20.7	337468	8190	673	229	519	248	5	52
-67	1	28.2	342646	1370	510	667	204	117	7	107
-68A	1	36.2	335012	1632	471	379	250	106	10	100
-68B	1	67.5	320433	1587	448	356	519	241	18	104
-68M	6	84.4	276230	2541	382	967	1825	384	36	380

[1] Species (SP) are: 1=<u>Composita</u>; 2=<u>Neospirifer</u>; 3=<u>Linoproductus</u>; 4=Crinoid; 5=Cement; 6=Matrix and 7=Unidentified fossil skeletons; [2] IR are reported in %;
[3] Elemental contents are measured in ppm except Cd, which is measured in ppb.

APPENDIX II

DATA OF STABLE ISOTOPE ANALYSIS, MADERA FORMATION, NEW MEXICO

SAMPLE	SP[1]	$\delta^{18}O$ (‰, PDB)	$\delta^{13}C$ (‰, PDB)
UL -1C	2	-4.51	-2.43
-2A[2]	4	-5.24	-5.14
-2B	1	-4.58	-1.46
-2BM	6	-6.56	-4.52
-2E	2	-4.08	2.26
-2EM	6	-5.20	-4.32
-4C	1	-4.24	3.10
-4D	2	-3.91	3.41
-4DM	6	-5.17	-3.57
-4G2	2	-3.71	2.87
-4GM	6	-5.33	-3.72
-4H1	1	-3.43	2.18
-4H2	1	-3.50	1.36
-5A	1	-4.27	-0.84
-5B	2	-3.86	0.51
-6A	1	-4.79	-0.80
-6B1	2	-3.60	3.29
-6C2	2	-4.58	0.39
MMA -1S	5	-6.59	-3.94
-2	1	-4.52	1.60
-4M	6	-5.44	-4.44
-5	1	-4.56	-0.40
-5S	5	-5.63	-3.84
-6	1	-4.99	-1.68
-6S	5	-6.08	-3.84
MMA -7	1	-4.26	-1.97
-9	1	-4.14	-1.36
-10	3	-3.82	-1.24
-10M	6	-4.93	-3.11
-11	3	-3.65	-2.38
-13	1	-4.38	-1.75
-14B	2	-4.32	2.08
-14M	6	-5.04	-4.38
-15	2	-4.07	2.55
UL -22	2	-3.88	2.90
-23	1	-4.07	2.77
-25M	6	-5.77	-4.54
-26	3	-4.05	-0.48
-31	1	-4.61	2.28
-34A	2	-5.59	2.60
-34B	2	-4.40	3.79
-35M	6	-5.75	1.87
BR -4	5	-4.88	-4.50
-5	1	-4.81	2.70
-11B	1	-4.06	2.90
-14A	1	-3.21	3.25
-15	5	-4.54	0.48
-16	5	-7.94	-0.56
-17	2	-3.56	3.50
-18	4	-6.41	1.16

SAMPLE	SP	$\delta^{18}O$ (‰, PDB)	$\delta^{13}C$ (‰, PDB)
BR -19A	1	-3.58	3.02
-19B	1	-2.90	4.17
-22B	2	-3.87	3.35
-22C	2	-3.79	3.26
-23S	5	-9.15	-0.76
-25A	1	-3.64	2.98
-25B	1	-4.27	2.63
-26	3	-4.41	-0.27
-27	3	-4.53	-0.40
-28M	6	-6.93	-1.10
-29A	3	-4.56	-0.21
-29B	3	-4.67	0.13
-29C	3	-4.74	0.41
-29D	3	-4.44	0.64
-29M	6	-5.93	-2.96
-31	3	-5.04	-2.11
-32M	6	-4.61	-3.06
-33	3	-4.47	-2.01
-34A	3	-4.40	-1.70
-36	3	-3.94	-2.30
-36M	6	-4.79	-3.25
-39	1	-4.08	2.60
-40	1	-4.11	-3.82
-40M'	6	-5.75	-2.07
-41A	2	-4.69	2.69
BR -42	3	-5.33	1.69
-43	2	-4.46	2.91
-45	1	-5.06	1.55
-46A	2	-4.60	3.02
-46B	2	-5.00	2.88
-46M	6	-8.68	1.21
-47B	3	-4.73	1.11
-47C	3	-4.36	0.79
-48M	6	-6.40	1.74
-49B	4	-5.07	2.14
-52A	2	-4.46	2.76
-52B	2	-4.07	2.93
-53A	1	-4.22	1.22
-55A	3	-4.60	1.91
-55B	3	-5.26	1.55
-55M'	6	-5.95	0.36
-56	1	-5.16	1.85
-57	1	-4.16	3.46
-57M'	6	-4.57	0.22
-59	4	-4.87	1.38
-61B	2	-3.99	2.88
-62	1	-4.62	1.99
-63	3	-4.57	1.58
-65	2	-4.29	3.06
-66	4	-4.61	1.56
-67	1	-4.45	0.62
-68A	1	-4.44	1.15
-68M	6	-7.45	-1.95

[1] Species (SP) refer to Appendix I; [2] The bold are duplicate samples and the number is in average.